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STUDY ON ENVIRONMENTAL IMPACT OF HIGHLY-PERFORMANCE ELECTRICAL INSULATION RESINS: SYNTHESIS OF NMP-FREE AND BIO-BASED WIRE ENAMELS

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AUTHOR'S DECLARATION

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for School of Advanced Studies, and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of others, is indicated as such. Any views expressed in the dissertation are those of the author.

Signed

Date

15/05/2022

ABSTRACT

The research reported in this thesis is the result of a strong partnership between the University of Camerino and ELANTAS Europe S.r.l. The strong collaboration between the university and several companies allows students to do research with an industrial approach and at the same time to face with challenges given by working life.

The work was carried out among the laboratory of Organic Chemistry of Prof. Enrico Marcantoni at the University of Camerino (Camerino, Italy) and the R&D laboratory of ELANTAS Europe in Ascoli Piceno (Italy). Elantas Europe is a leading manufacturer of insulating and protective materials. In the site of Ascoli Piceno, Elantas Europe manufactures high-performance enamels for use as magnet wire coatings. They are coated on the surface of copper or aluminum wires and cured to form an electrical insulation film. Magnet wire enamels, in general, consist of polymeric resins dissolved in organic solvents. Apart from the basic electrical insulation requirement, this means, depending on the end-use application, wire enamels provide high thermal and mechanical stability, flexibility, moisture resistance, and long service life of the insulation. The main end use application areas are transportation, automotive, household appliances, motors, transformers, industrial electronics, or power generation.

The work made in these three years concern the environmental impact of some industrial polymeric materials. In particular, the aim of the work was to replace the well-known and most used solvent in wire enamel, *N*-methylpyrrolidone (NMP), with a safer and greener solvent in polyamide-imide (PAI) and polyimide (PI) precursor, that is, polyamic-acid (PAA). In addition, a part of the thesis concerns the synthesis and characterization of polyimide precursor and polyester-imides (PEI) wire enamel using bio-based diamines (obtained from fatty acid dimers) replacing totally 4,4'-oxydianiline (ODA) and 4,4'diaminodiphenilmethane (MDA). Chemical structure, molecular weight distribution, thermo-mechanical and electrical properties of obtained polymers were determined and discussed. This work was carried out almost entirely in R&D laboratories of Elantas Europe plant in Ascoli Piceno.

A second part of the thesis work was carried out in the laboratory of organic chemistry of Prof. Enrico Marcantoni at the University of Camerino, chemistry department. The work was focused on the development of an innovative method for the determination of residual isocyanate monomers in different batches of solvent-based polyamide (PA) resin.

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List of Abbreviations

ATR: attenuated total reflectance

BD: bio-based diamine

DI: diisocyanate

DIDA: diimide-diacid

GPC: gel permeation chromatography

MDA: 4,4’-methylenedianiline

MDI: methylene diphenyl diisocyanate

MDPA: 3-methoxy-*N*,*N*-dimethylpropionamide

MEG: ethylene glycol

NFM: *N*-formylmorpholine

NMP: *N*-methyl-2-pyrrolidone

ODA: 4,4’-oxydianiline

PA: polyamide

PAA: polyamic-acid

PAI: polyamide-imide

PEI: polyester-imide

PI: polyimide

PMDA: pyromellitic dianhydride

PU: polyurethane

SC: solid content

THEIC: tris(2-hydroxyethyl) isocyanurate

TMA: trimellitic anhydride

TMAC : trimellitic anhydride chloride

TPA: terephthalic acid

WE: wire enamel

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PART I

THEORY

The background of magnet-wire insulating system and its application is discussed herein, followed by a brief discussion of wire enamels classification and finished product testing procedures. Afterwards, the focus will shift to the chemical point of view of wire enamel composition, their synthesis and characterization.

1. Wire Enamels

In this chapter wire enamels will be introduced and explained, followed by an examination of coating technology and main performance indicators as well. Chemistry of such resins will be addressed more specifically in chapter 2.

1.1. Introduction

There are dozens and dozens of electrical devices that impact our everyday life. We are surrounded by them in our house, in our car and in our workplace. In private houses, electrical machines power every home appliance, transformers are needed to charge phone batteries, run TVs, computers and many other devices. Electrical motors power the windows of cars, help adjust the seats, mirrors and headlights. They constitute the main organ of propulsion in electric and hybrid vehicles. In industry, large transformer units convert the high currency from power plants into standard AC voltage and the kinetic energy obtained by traditional power plants as well as by wind turbines into electricity.

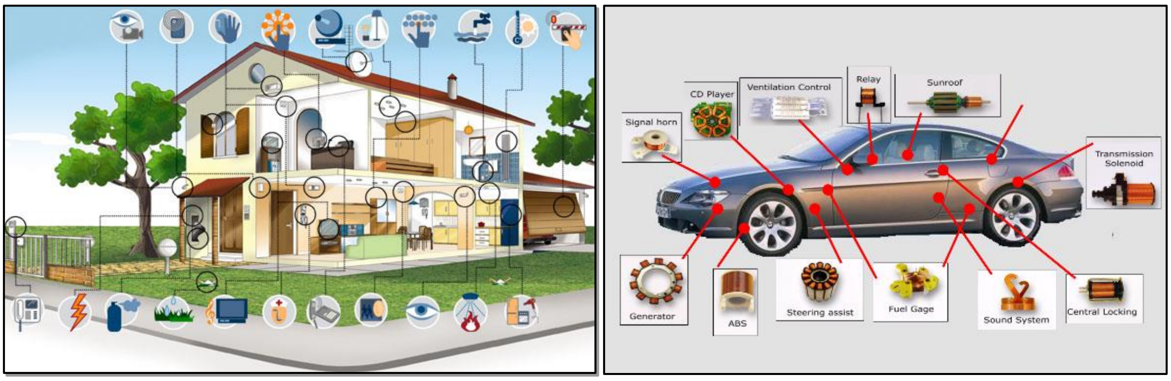


Figure 1. Electrical devices in a smart house and in a car. Note: from Elantas internal database.

To build functionary electrical devices and machines, it is necessary to generate electromagnetic fields by guiding the electric current in defined ways. This task is achieved using wire coils, made of a conductive material, that is, in the majority of cases, copper. Copper wires must be insulated in order to force electric current to run in a defined way, and not in the way of lowest resistance. The easiest way to obtain this is by leading the conductors at a distance from each other which is greater than the flash-over distance of the tension. This principle is still in use with printed circuits, but it can hardly be used in an electrical motor or generator.

Such machines would be extremely large and very difficult to run effectively, hence, the insulating medium (air) has been substituted by polymeric material, thus creating the so-called enameled magnet wires, allowing copper windings to be brought into very close contact without short-circuiting.

Although described as “enameled”, enameled wire is not, in fact, coated with a layer of enamel paint or vitreous enamel made of fused glass powder but with a thin layer of polymer film insulation. Wire enamel is, in most cases, a mixture of oligomeric structures diluted in a solvent system with latent catalysts, cross-linkers, and special purpose additives, that is coated (or enameled) on wires making them electrically insulated, therefore able to generate the magnetic field necessary to make the electric device work. During the enameling process, solvents evaporate, oligomers react with each other into an insoluble and infusible macromolecules, forming a cured film on the wire surface (Figure 2). The resulting film is characterized by specific properties, depending on the chemical nature of the enamel and on the enameling conditions. In many cases the development led to a dual coat system, one as base-coat and the other as top-coat. Base-coats generally show good adhesion to the copper and high flexibility and topcoats lead to high abrasion and higher temperature resistance.

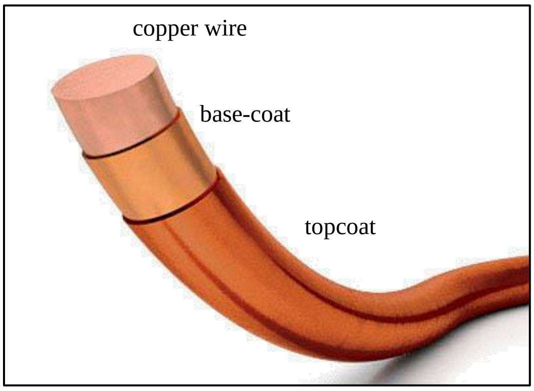


Figure 2. Section of an enameled copper wire. Note: from Elantas internal database.

Enameled wires are then used for different applications; when used for electric motors, or where wear conditions are high, they are also exposed to friction, abrasion, humidity, and often rotational forces. To protect and extend the lifetime of these components, impregnating agents based on alkyl, phenolic, epoxy or unsaturated polyester resins are applied on electrical devices providing mechanical support, protection against excessive movement, improvement in heat transfer and thermal endurance (Figure 3). This is called secondary insulation.

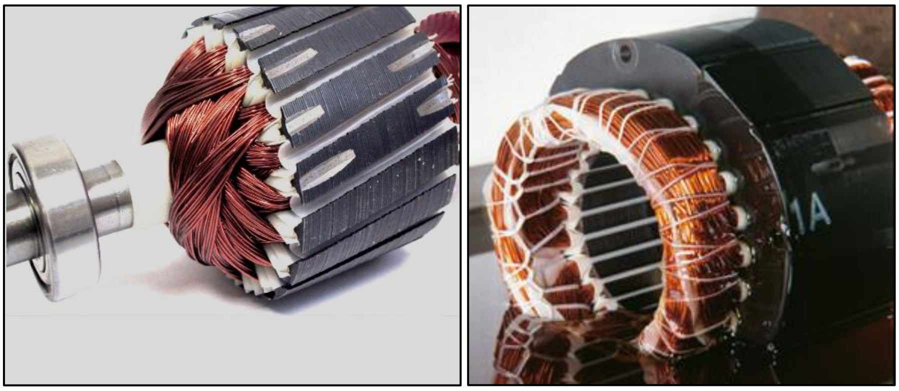


Figure 3. Components of an electrical motor: the enameled magnet wires are winded inside a rotor (left) and in a stator (right). Note: from "https://www.elantas.com/.

1.2. Development of magnet wire insulations

The history of electro insulating coatings starts in the 19th century, when natural fibers of cellulose, silk, flax, cotton, wool, and, later, asbestos were used to wrap and insulate wires of stators and rotors of the first dynamo-machines invented by Siemens. Fibrous materials had the big problem to be hygroscopic so that the isolation properties were dramatically reduced after moisture absorption. Later, at the very beginning of 20th century, other materials were adopted to prevent such problem, like oil bitumen, giving rise to the so called "black enamel", followed by copal originating the so called "blond enamel".[1] Such products were natural materials, therefore the consistency of batches was poor. Around 1915, enamels based on synthetic materials such as phenolic resins gradually substituted natural resin-based varnishes: they made it possible to cover the wires directly without having to insulate the wires with fibrous materials first. Very successful was the use of polyvinyl-acetal (PVA) based varnishes (Formvar®), developed in 1938 by Hoechst and General Electric.[1-2] In 1940, varnishes based on polyamide (nylon) were introduced. Three years later (1943) terephthalic polyester-based varnishes were simultaneously introduced by General Electric in the USA and Dr. Beck in Germany.[3-4] In the 1950s, polyurethane, polypropylene, and polycarbonate were introduced.[5] Although the early versions of these materials often lacked the sophistication and property enhancements of current offerings, their arrival on the scene led to an explosion of new applications in electrical insulation. In the same years, the concept of using two different coatings was developed; the first dual-coating was made available in 1953 when a polyamide film was applied over Formvar, polyester, polyurethane, and acrylic films to lower surface friction, improving resistance to mechanical damage during high-speed winding. Polyester-imides were for the first time developed in the early 60's of the last century by Dr. Beck & Co GmbH and were born with the intent to merge the good mechanical properties of terephthalic acid polyesters, used as copper wire coatings since the middle 50's, with the excellent thermal resistance of polyimides, introduced as wire coating by DuPont during the same years, avoiding processing limitations connected with polyimides.[6-7] Polyamide-imides where commercialized in the late 60's by Amoco.[8] In the same years, a new branching agent was introduced by Schenectady, which could further improve mechanical and thermal properties of resulting polymer: tris(2-hydroxyethyl) isocyanurate (THEIC) (IUPAC name: 1,3,5-Tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione). The new generation of THEIC-modified polyester-imides was born, which is still nowadays the top performing version of polyester-imides.[9]

The history of wire enamels is summarized Table 1.

Table 1. History of wire enamels.

Year	*Chemical basis*	*Inventor*	*Properties*	*Importance today*
1900	Oil-bitumen		Excellent humidity resistance, poor thermal properties	None
1915	Tung oil, copal, phenolic resins		Improved hardness, flexibility and solvent resistance	None
1938	Polyvinyl acetal	General Electric	Excellent mechanical properties and adhesion, low solids	Reduced
1940	Polyamide		Improved mechanical properties, flexibility, low coefficient of friction, self-bonding	Overcoat, self-bonding
1950	Polyurethane	Bayer	Solderable, fast enameling	Many
1954	Polyester (glycerin)	General Electric, Beck	Excellent solvents and humidity resistance, good thermal endurance	Reduced
1959	Polyimide	DuPont	Outstanding thermal resistance, high raw material costs	Special application
1961	Polyester-imide (glycerin)	Beck	Improved cut through and thermal endurance, increased enameling speed	Reduced
1965	Polyester-imide (THEIC)	Schenectady	High cut through, hydrolytic stability, Freon resistance	Great
1966	Polyamide-imide	Amoco	Excellent thermal, mechanical properties	Great
1967	Polyester (THEIC)	Schenectady	Improved thermal endurance, adhesion, base coat in dual coat systems (PAI as overcoat)	Great
1968	Polyhydantoin[10]	Bayer AG	Excellent thermal properties and adhesion, high raw material cost	None
1973–1980	Alternative enameling technologies	Beck, Herberts	Hot melts, water and mild solvent enamels, dispersion, powders, extrusion resins, Electrophoretic enamels	None
1988	Corona resistant wire enamels[11]	General Electric	Resistant to partial discharges in inverter driven motors	Special applications

The global wire enamel market is expected to grow significantly in the coming years, mainly thanks to advances in the transmission and distribution sector. The main emerging market trends facilitating growth are the growing solar energy industry, increased investment in smart grids and the adoption of energy efficient motors. The growing trend of miniaturization, the growing demand for greater efficiency and sustainability, and technological capabilities are expected to provide new market opportunities. Strict government regulations on VOC content are pushing producers to go green and embrace sustainability. Key players are infusing high investments in research and development to develop innovative and novel products that can be offered at low cost in compliance with regulatory guidelines. However, high formulation costs, unstable raw material costs, and strict government regulations on VOCs pose a significant challenge to market participants. Today, global production of wire enamels is around 300,000 tons per year. The resins used are primarily: polyester-imides (PEI), polyurethanes (PU), polyester (PES), THEIC-modified polyesters, polyamide-imides (PAI), polyvinyl-formals (PVF) (see Table 2 and Figure 4).[12]

Table 2. Wire enamel market by product type.

Product	***Abbreviation***	***Market share***
Polyester-imide	PEI	30 %
Polyurethane	PU	20 %
Polyester	PES	18 %
THEIC-modified polyester	THEIC PES	10 %
Polyamide-imide	PAI	10 %
Polyvinyl-formal	PVF	7 %
Self-bonding wire enamel	SB	4 %
Others		1 %

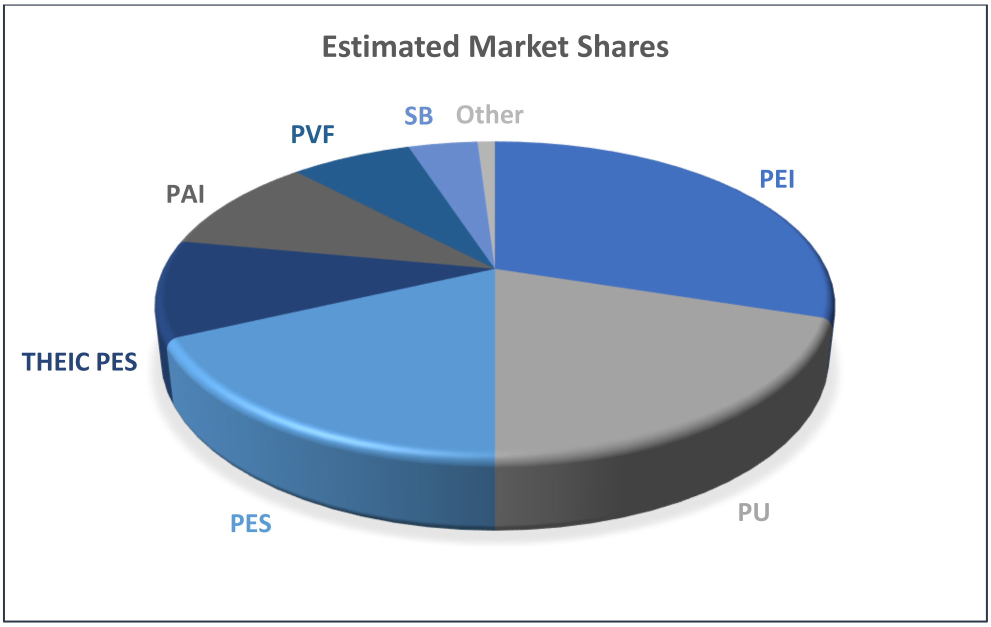


Figure 4. Estimated market shares today.

The market for electric motors is dominated by THEIC-modified PEI or THEIC-modified polyester coatings with PAI topcoat. The THEIC PEI or polyesters show good adhesion to the copper and high flexibility, and the PAI topcoat leads to a high abrasion and high temperature resistance. Power tools, ceiling fans, appliances, air moving motors, hermetic motors for cooling and refrigeration, and electric motors in automobiles, all use this technology.

The magnet wire market in automobiles varies dramatically, Solenoids, motors, starters, generators and other electrical components have specialized needs of magnet wire coatings. The predominant coatings, however, are polyurethanes.[13]

1.3. Magnet wire enameling technology

The enameling stage is a necessary step for research because until now, it is the only and actual way to evaluate the quality of products. Only by testing the properties of the enameled wire, it is possible to evaluate the goodness of the enamel.

To apply an enamel means allowing to the molecules of the latter to react with each other, forming a three-dimensional network. Thus, the layer formed will give the desired electrical, mechanical, chemical and thermal resistance to the wire. The manufacture of a good enameled wire involves a proper application of the enamel to the wire. In order to get such result, an enameling machine, or oven, is used. The enameling oven is able to apply liquid enamels to the wires and cure them to create a solid film around the wires. Wire enamels must be processable to be applied and cured on wires. This means that their viscosity and solid content must stand within a range of values. More important, the solution must be homogenous without precipitates or gels.

Depending on the diameter of the wire, on the viscosity and the solid content of the resins, the latter are cured in vertical or horizontal ovens. Vertical ovens are preferred for big diameters (both round and flat wires) and varnishes with medium-high viscosity (2000-10000 cPs at 23°C) which are preferred, while horizontal ovens are used for medium-fine wires where low-medium viscosity varnishes (100-2000 cps at 23°C) are preferred wires.

Different applicators can be used (dyes or felts), also depending on the diameter of the wire and the viscosity of the resins. Dyes are preferred for medium-big diameters wires (> 0,2 mm) where the viscosity of the enamels is usually > 200 cPs, while felts are used for fine wires (with a diameter 0,05 – 0,2 mm), where the employed varnishes cannot be too viscous (viscosity < 200cPs).

Figure 5. Horizontal enameling machine. Note: from Elantas internal database.

In both ovens configurations, the application procedure is identical: the first step is the annealing and cleaning of the bare wire which occurs at high temperatures and in a reducing atmosphere of steam with the aim to soften the copper wire making it more malleable, but also to eliminate dirt and oils. Subsequently, the enamel is applied to the wire surface with dies or felts (Figure 6) immediately prior to passing through the oven chamber more than one time. This process is mainly called “curing step” where in sequence occur:

- evaporation of solvents;
- increase in the molecular weight of polymer chains;
- cross-link reactions: it only occurs in polymers where reactive functionalities are present along chains and/or crosslinking agents are present;
- intra-chain reactions: e.g. ring closure reactions.

The oven temperature ranges from 500 to 700°C. Six to eight coats of enamel are applied, with individual coats of the order of 0.002 to 0.005 mm in thickness. Multiple coating ensures that tiny blow-holes and bare spots, caused by rapid solvent vaporization and poor wetting, respectively, are covered by subsequent coats, making the numbers of defects of the wire enamels film near to zero. In addition, thin films can be cured quickly, allowing the enameling speed to be increased significantly. [14-15]

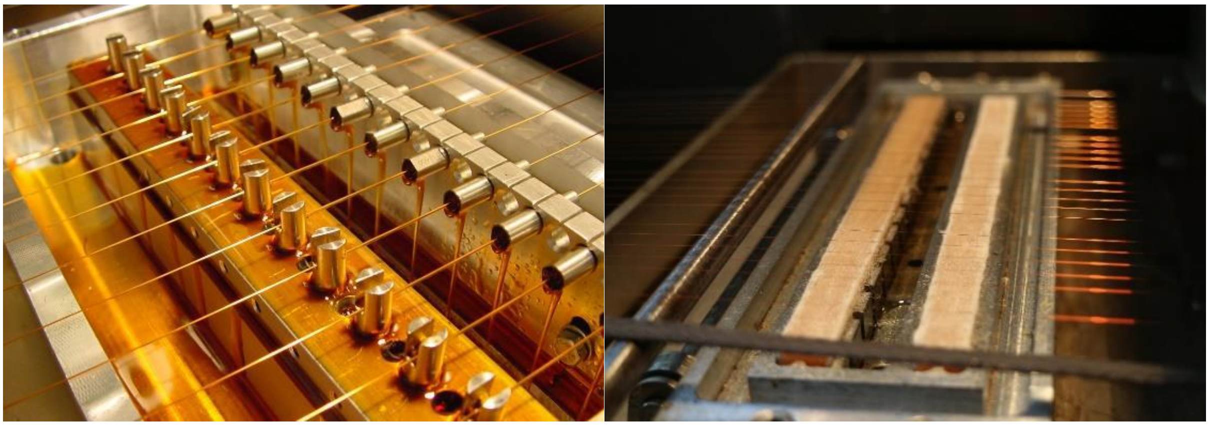


Figure 6. Applicators with dies (left), applicators with felts (right). Note: from Elantas internal database.

Enameling machines are designed with air-recirculation system and catalytic ovens able to oxidize solvent vapors to CO_2 and steam (Figure 7). Solvent out-gases from the varnish are passed over a heated (up to ≈ 600°C) catalyst mesh, and the exhaust is recirculated to the oven inlet, providing additional heat. These ovens are the most energy efficient and reduce levels of noxious fumes exhausted into the atmosphere.

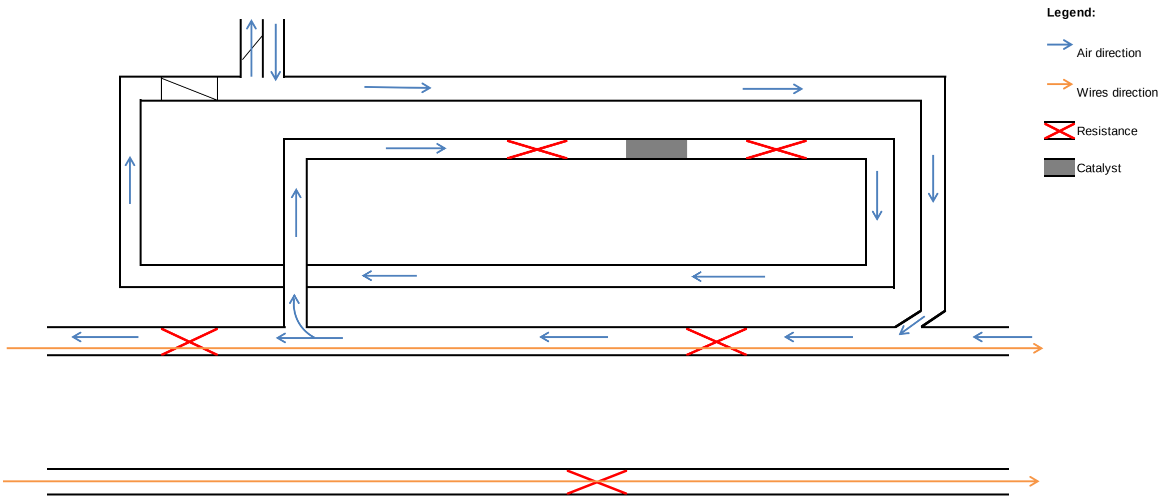


Figure 7. Schematic view of an enameling oven.

Once the desired thickness is reached, the enameled wire goes to a first spooler where it winds up to a spool. A second spool allows switching and winding up the wire on both spools alternatively, so that one can take a sample without stopping the machine (Figure 8).

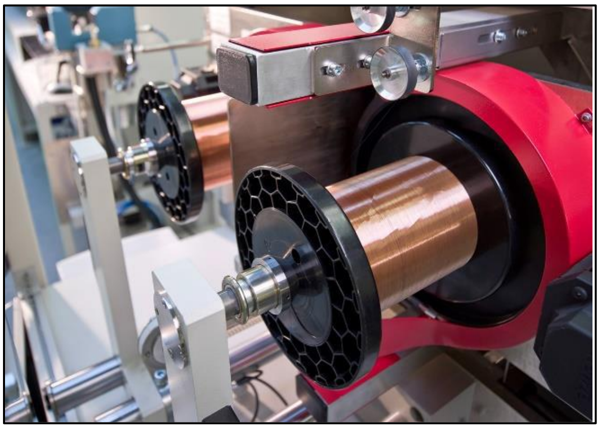


Figure 8. Spooler. Note: from Elantas internal database.

1.4. Main Properties and Evaluation Tests

Once the enamel has been properly applied and cured on the wire, the resulting conductor – coating system is characterized by specific properties, therefore the enameled wire is checked for quality characteristics. The aspect of the insulation is detected by checking the wire with a microscope. This is a qualitative inspection, which delivers a pass/non pass result, though arbitrary ranking can be assigned by enamellers. In Elantas wires are classified from zero to three based on the presence of blisters, waves and dots, the higher the worse. A uniform thickness of the enamel layer is also checked. The thickness is measured in different points of the sample using a micrometer. The thickness must be as uniform as possible to guarantee an excellent performance and properties reproducibility, especially when they depend on coating thickness.

To ensure that users can compare materials from different manufacturers, properties of enameled wires have been standardized by international standardization commissions like IEC (International Electrotechnical Commission), UL (Underwriters Laboratories), ISO (International Organization for Standardization), IEEE (Institute of Electrical and Electronic Engineers) and many national standards organizations like NEMA (National Electrical Manufacturers Association), DIN, EN, BS, CEI, NF, AS, JIS, IS etc. Among these, the most widely accepted International Standards are those ones developed and approved by IEC. [16]

According to the standard commissions, the properties of enameled wire can be divided into four main types:

- Mechanical

- Thermal
- Electrical
- Chemical

1.4.1. Mechanical properties

Wires are subjected to mechanical stress when winding for the manufacture of electrical devices. For example, upon motor winding, the copper wire can stretch up to 10% and the insulating film must be able to tolerate this elongation and still maintain adequate adhesion and electrical properties without scrapes.

According to the International Electrotechnical Commission (IEC 60317), these properties can be summarized into:

- Elongation

It is the increase in length expressed as percentage of the original length.

- Springiness

It is the recoil measured in degrees after the wire is wound in the form of a helical coil or bent through an angle.

- Abrasion resistance

It is the maximum force which can be sustained when a needle scrapes along the wire under a progressively increasing force. It can be tested both with «unilateral» and «bidirectional» tester. In both cases the wire is peeled off at one end while the other one is kept under stress. A needle is permitted to go in one or both directions (according to the test type) scratching the enamel until it reaches the bare copper. The test is repeated on 3 sides of the specimen.

- Flexibility and adhesion

It is the potential of the wire to withstand stretching, winding, bending, or twisting without showing cracks or loss of adhesion of the insulation. After a given amount of elongation (5 to 25%) applied through «elongation to break test» (Figure 9, left), the wire is wound around a mandrel (Figure 9, right) with stepwise defined diameters (1 to *n* times the wire diameter). The appearance of cracks and loss of adhesion are visually checked. These characteristics are directly related to the strain applied to the wire during the automatized winding of an electrical machine.

Figure 9. Wire elongator (left) and mandrel (right).

Another way to test adhesion is through a peel test (Figure 10): in this test one half of the enamel coating is removed with a cutter. The wire is then twisted until the enamel peels from the copper surface. The number of revolutions required for delamination is recorded. The test is typically run-on wire before and after thermal aging.

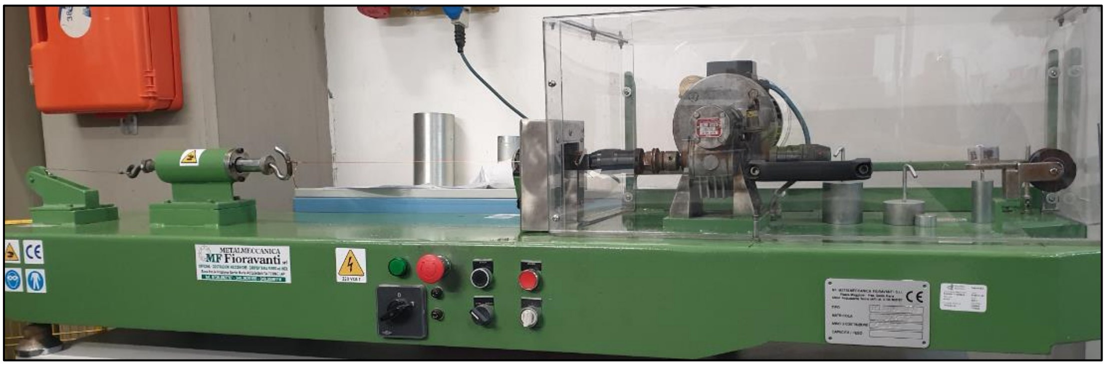


Figure 10. Wire twister.

In addition, before any kind of test, the enameled are also subjected to a “jerk test”: it consists in manually snatching the wire and checking the appearance of cracks and loss of adhesion near the point of rupture of the wire (Figure 11). This preliminary test delivers a pass/non pass result.

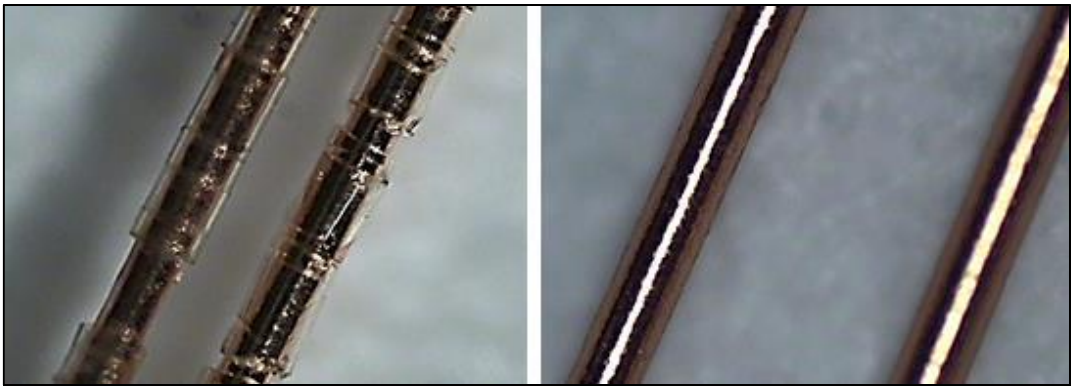


Figure 11. Jerk test results: "not passed" (a) and "passed" (b). Note: from Elantas internal database.

1.4.2. Thermal properties

Electric and electronic devices are subjected to thermal stresses generated by external conditions or, more often, by the Joule heating due to electrical conductor's residual resistance and friction of moving components. Examples are high performance electric motors or high voltage A/C – D/C transformers which are located in a confined and thermal-isolated space. These conditions must be managed by magnet wires to avoid short-circuiting due to softening or thermal degradation of the polymeric film. Thermal properties must be tested in order to ensure an adequate lifetime of the finished product. Thermal properties describe the capacity of the enamel to maintain its structure and properties at high temperatures. Typical wire tests are:

- Thermal class

The thermal class or heat classification is expressed as "temperature index". It defines the temperature at which the insulating film will withstand a defined voltage for 20,000 hours. To avoid long test times, an accelerated test procedure takes place. Wire samples are aged at different temperatures, higher than the expected class temperature. The failure time is periodically checked at room temperature under a defined voltage (e.g., 1,000 V for a 1 mm diameter wire). These values are extrapolated to 20,000 h using the Arrhenius law to find the thermal index of the wire enamel.

- Heat shock

The same test sample used to determine the flexibility is heated at a specific temperature according to its thermal class and then cooled to ambient temperature. No cracks must be visible. This property is related to the capability of the winding to resist against thermal shocks.

- Cut-through

Two specimens of the magnet wire are placed into a hot plate and set in a perpendicular cross section so that they touch each other in one point where a standard weight is placed. The test consists in determining the maximum temperature at which the two metal parts of the wires do not get in contact (short circuit) in less than 2 minutes. This test is correlated to the flowing capability of the enamel under pressure. Modern enamels with a thermal class of 200°C have cut-through temperatures higher than 320°C. This value allows an estimation of the existing safety margin of a winding in case of a hot spot.

This test will be performed on magnet enameled wires accomplished in this work.

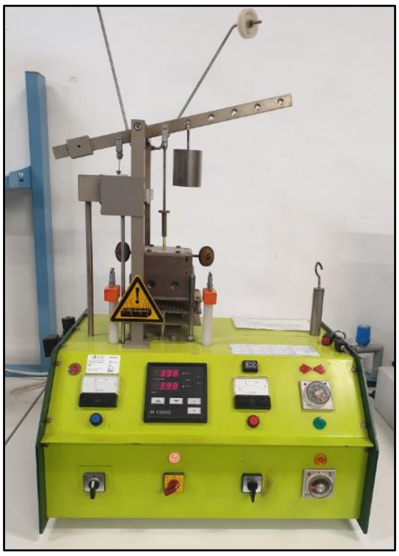


Figure 12. Cut-through tester.

1.4.3. Electrical properties

Electrical properties are related to the capacity of the enameled wire to withstand electrical field (electrical resistance, dielectric loss tangent) and voltage (breakdown voltage, continuity of covering) generated by the current passing through the conductor. According to the International Electro-technical Commission (IEC 60317), they can be summarized into:

- Breakdown voltage (BDV)

A wire twist pair is prepared as specimen and put in the tester. The voltage, with a nominal frequency of 50 or 60 Hz, is increased until breakdown. The breakdown voltage indicates the maximum A.C. voltage that the enamel can withstand without breaking down, i.e., without experiencing failure of its insulating properties. This property is thickness and material dependent.

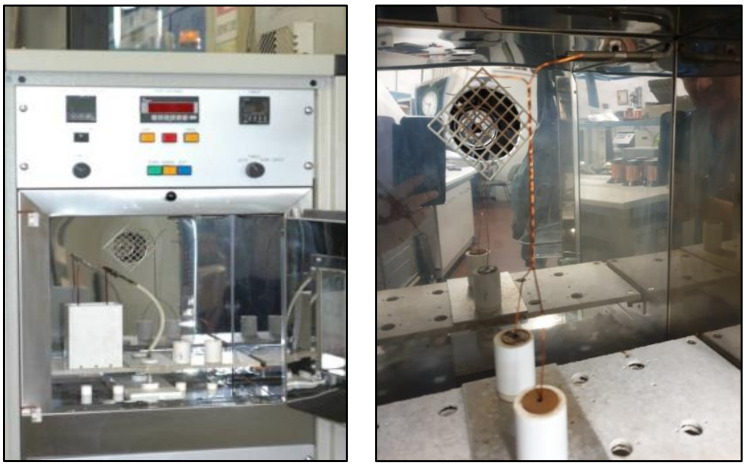


Figure 13. Breakdown voltage tester and a detail of the instrument.

- Continuity of covering

The uniformity of coating is measured under a specified potential difference.

- Dielectric loss tangent or tangent delta (Tgδ):

The magnet wire specimen is covered with graphite in order to create a condenser where the enamel represents the dielectric.
This test will be accomplished on finished batches performed in this work.

Figure 14. Tangent delta tester.

The dissipation factor (CoD) is plotted vs. the increasing temperature. When the dissipation factor increases dramatically, the intersection point at the tangents of the obtained curve gives the correspondent temperature (indicated as “Tgδ”) at which the material stops retaining a low

CoD (i.e., the dielectric properties have been lost). The tangent is an indication of the loss of dielectric properties and is related to the glass transition temperature. It is used as a measure of cure for magnet wire production.

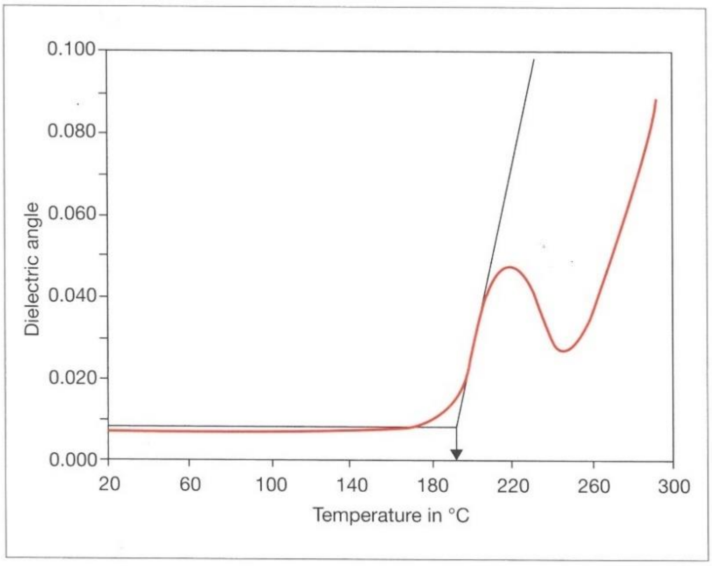


Figure 15. Example of tangent delta test result. Note: from Polymers for Electrical Insulation: Coatings and Casting Materials for the Electrical Industry.

1.4.3.1. Chemical properties

Chemical properties are related to the capacity of the enamel to withstand attack by chemicals. Resistance to chemicals is desirable to prevent electrical breakdown of the film caused by the absorption of solvent or oils present in some electrical devices to prevent damages from corrosion or friction of the moving parts. According to the International Electrotechnical Commission (IEC 60317), they can be summarized into:

- Resistance to solvents

It measures the capacity of the wire to retain its hardness after remaining in a specified solvent mixture. The wire is put into a solvent mixture (e.g., butanol, styrene, white spirit and xylene) at a specific temperature for a given time, after which the wire undergoes a hardness test by scratching it with different pencils at decreasing hardness. The resistance is given by the code of the pencil at which the enamel resists. For solvents like ethanol, a visual check of eventual micro rings formation on the wire coating is checked at the microscope. The latter test does not belong to the IEC standards.

- Resistance to refrigerants

It is expressed as percentage of retained mass after treatments with refrigerants like Freon R22, R134 etc.

- Resistance to transformer oil

It is a measure of breakdown voltage and loss of adhesion of enamel after the wire has been heated in wet transformer oil in a sealed system. Three specimens of the wire are placed into a calorimetric bomb containing oil normally used in transformers and kept at a specific temperature (e.g., 150°C) for a given time (from few days to several weeks). The wires are then checked for appearance and retained BDV.

- Solderability

In this test, the specimen is immersed into a solder bath containing a metal alloy kept at specific temperatures (e.g., 320°C or 370°C) until the enamel is destroyed. The necessary time before solder formation gives the solderability value of the enamel.

For this work, only mechanical (jerk test, flexibility) thermal (cut-through) and electrical (Tgδ) tests will be performed.
A comparison of different wire enamel types is displayed in the following table.

Table 3.Comparison of advantages and disadvantages of different wire enamel types.

Product	*PVF*	*PE*	*THEIC-mod PE*	*PEI*	*THEIC-mod PEI*	*PU*	*PAI*	*PI*
1. Mechanical values								
Flexibility	+ + + + +	+ + + + +	+ + + + +	+ + + + +	+ + + +	+ + + +	+ + + +	+ + +
Adherence	+ + + + +	+ + + + +	+ + + + +	+ + +	+ + + +	+ + + +	+ +	+ +
Abrasion resistance	+ + + + +	+ + +	+ + + +	+ + + +	+ + + +	+ + +	+ + + + +	+ + + + +
2. Thermal values								
Temperature index [°C] [a]	≤ 120	120-150	155-200	≤ 155	180-200	155-180	≤ 220	≥240
Cut-through [°C]	250-290	320-350	410-450	330-380	390-440	200-260	390-420	> 550
Heat shock [°C]	≤ 180	≤ 180	≤ 220	≤ 180	≤ 180	≤ 200	240	> 260
3. Electrical values								
Tangent delta [°C] [b]	≤ 110	110-140	150-175	160-190	175-215	130-180	260-280	280-290
Breakdown voltage [V·µm]	120-150	90-110	120-1510	110-130	130-160	120-150	150-190	150-190
4. Chemical values								
Resistance to solvents	+ +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + + +	+ + + + +
Resistance to refrigerants	+ + + + +	+ + +	+ + + +	+ + +	+ + + +	+ + +	+ + + + +	+ + + + +
Resistance to transformer oils	+ + + + +	+ +	+ + +	+ +	+ + + +	N.A.	+ + + + +	+ + + + +
Solderability [c]	+ +	+ + +	-	+ +	-	+ + + + +	-	-
+++++ *excellent;* ++++ *very good;* +++ *good;* ++ *acceptable;* + *poor*								

[a] according to IEC 60172. [b] Dansk method. [c] At 470°C, special formulation.

2. Chemistry of Wire Enamels

A coating is a covering that is applied to the surface of a substrate. The purpose of applying the coating may be decorative or functional. For an industrial point of view, the first aim is the functionality, but even the eyes take their part. Functional coatings are applied to change the properties of the substrate: such as adhesion, wettability, resistance to chemical or mechanical stress, conductibility, insulation. There are several types of coating. They can be discerned by their physical state (liquid, gas or solid) and/or by their application method: chemical or physical vapor deposition, chemical and electrochemical techniques, spraying, roll-to-roll process and many others. Varnishes and enamels are part of the coatings, and they could be liquid, as organic solvents solution (sometimes aqueous solution), or solid, as solvent-free resins.

A general organic enamel composition consists of:

- Binders

Binders are generally solid, sticky materials that hold the system together. They are also called binders and, when in a solvent, they are the vehicles for the system. They constitute most of the solid content of the coating system and determines, to a large extent, the properties of the coating film

- Volatile components

Solvents permit to apply the coating in a liquid state. They may be organic or even be water. They are in the formulation to aid in mixing, viscosity, workability and application of the coating. After application, they evaporate and leave a dry film.

- Catalysts

They are organic or inorganic molecules that accelerate the polymerization reaction.

- Additives

These are ingredients added in small (<5%) amounts to improve some properties of the coating. They could be, for example, plasticizers or leveling agent.

- Pigments

They are the dry materials added to the coating to give it color or resistance properties, camouflaging properties and the like. Pigments can be divided into many different categories for different purposes. Some materials are primary pigments versus filler pigments. Some materials are organic in nature, and others are inorganic. Properties such as lightfastness, particle size and specific color are reasons for choice

- Crosslinkers

Crosslinking is a very important process in coating film formation. The structure of the formed network determines the application properties of the coating film. Crosslinking agents are added to link together the polymer chains through ionic or covalent bonds to form a network which give, on the cured film, the desired properties. They may be long or short molecules, and they must be able to perform through their functionality, a proper crosslinking grade to improve the electrical, mechanical, thermal and chemical properties. There are two categories of crosslink agents.

1. Functional segments inserted in the main polymer chains.
2. Specific molecules added in a separate processing step, after that the linear (or branched) polymer is formed.

With network polymers, it is common to speak of crosslink density that is the number of crosslinked monomer unit per main chain. The higher is the crosslink density, the more rigid and is the polymer. Very high crosslink densities lead to embrittlement. Crosslinking reduces segmental motion; it is frequently employed to increase the glass transition temperature.

2.1. Binders

In this chapter, a deep focus on properties and synthetic routes of the binders used in my works will be addressed. The list includes polyamide-imide (PAI), polyimide (PI) precursor, hence, polyamic-acid (PAA) and at the end, polyester-imide (PEI).

2.1.1. Polyamide-imide

2.1.1.1. Properties and applications

In magnet wire coatings, adequate thermal, mechanical, and electrical properties must be maintained. One such polymer, mainly used as primary insulation, is polyamide-imide (PAI). PAIs are versatile high-performance polymers and are known for their outstanding thermal performance (high continuous use temperatures, high glass transition temperature, inherent flame resistance), excellent strength and stiffness, wear resistance, chemical and abrasion resistance, and low coefficient of friction.[17-19] PAIs have been developed as an alternative material for PIs and PAs with a promising balance of thermal stability with processability. These polymers combine the superior mechanical properties associated with the amide group, and the high thermal stability and solvent resistance of the imide ring in the same material, thus making the material even stronger.[20] Polyamide-imides have a decomposition onset at 500°C and the UL *relative thermal index* (RTI) predicts 100,000 h of useful life at temperatures up to 220°C.[21]

These properties enable PAI’s general use as insulating coatings for magnet wires, foils and circuit boards.[22-23] They can be also used in applications like filtration and biomedical applications (surgical instruments, instrument components and parts that require tight tolerances and dimensional stability). [24] PAI is also used in decorative, corrosion resistant coatings for industrial uses, often in conjunction with fluoropolymers: they aid in adhering the fluoropolymer to the metal substrate in non-stick cookware and bakeware coatings. Excellent bond strengths are observed with stainless steel, aluminum and titanium alloys, and PI films. [25-26] Other typical uses include advanced applications, such as in the electrical, aerospace, automotive, microelectronics, telecommunications, and energy fields in the form of adhesives, composite and coating materials.[27] Polyamide-imides, due to their relatively higher cost compared to common engineering plastics such as nylon and polycarbonate, are used when the application conditions require the property advantages of these materials and where minor polymeric materials would fail. They have a great strength-to-weight ratio as well and, for this reason, often used for metal replacements.

Aliphatic poly(amide-imide) resins were first reported by Frosch in 1942.[28] He used tricarballylic acid and an aliphatic diamine to prepare a polyamide-imide resin. The low thermal properties of the resulting PAI resin never allowed commercial utilization. DuPont was granted the first patent utilizing aromatic monomers.[29] This patent involved the reaction of trimellitic anhydride with aromatic diamines such as methylenedianiline. Amoco chemists were the first to commercialize PAI resins in the 1960s.[8] The initial application was in the electrical insulation market. The breakthrough was the ability to manufacture cost effectively trimellitic acid chloride from 1,2,4-trimethylbenzene. Reaction of the latter with aromatic diamines such as methylenedianiline and oxydianiline yields polymers that are of high quality for the electrical insulation market and extrusion resin market as well.

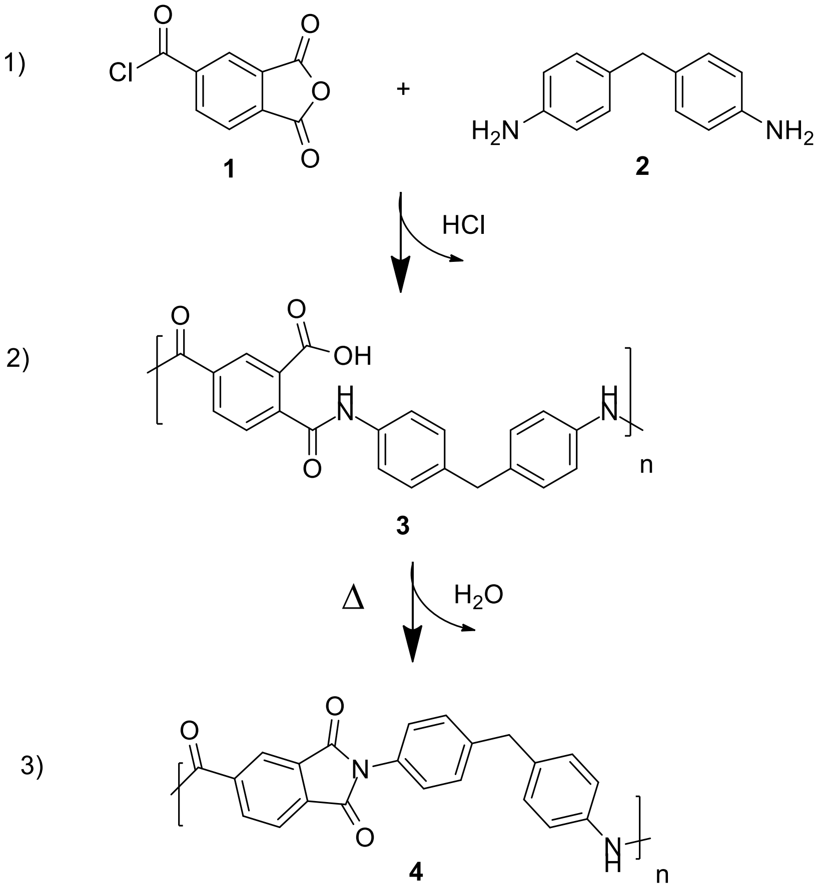
2.1.1.2. Synthetic routes

There are currently two popular commercial methods to synthesize polyamide-imides. One is the acid chloride route, and the other is the isocyanate route. The synthesis method used will determine and limit to some extent the applications in which the resultant polymer is used. The chemistry of these two methods is outlined below.

a) Acid chloride route

The earliest route to PAIs is the well-known acid chloride route. Acid chlorides are organic compounds composed of a chlorine atom attached to an acyl group, with the formula -COCl. They are reactive derivatives of carboxylic acids. The acid chloride family belongs to a large organic family called the acyl halides. These ones are organic compounds that have an acyl group attached to a halide group.

Polyamide-imides are prepared from a two-step process involving the condensation of trimellitic anhydride chloride (TMAC) and an aromatic diamine such as such as 4,4’-oxydianiline (ODA) or 4,4′-methylenedianiline (MDA) in a polar aprotic solvent, such as *N*-methylpyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAc) or dimethylsulfoxide (DMSO) at temperatures between 20 and 60°C (Scheme 1). [30-33]



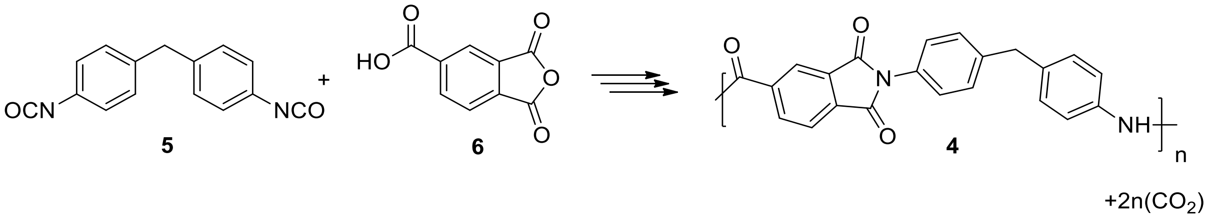
Scheme 1. Acid chloride route.

The polyamic-acid intermediate (Scheme 1.2) is stable and may be isolated as such. Acid chloride is produced as byproduct and must be quenched. The intermediate resin could be applied and cured where thermal treatment (Scheme 1.3) increases the molecular weight and imidization level and releases water. In addition to thermal treatment, polyamide-imides can subsequently cyclize through chemical imidization. The chemical treatment is accomplished by using an anhydride and a tertiary amine: typically, triethylamine and acetic anhydride are common, while other variants have also been used with success.[34-37] Low moisture levels are required to avoid early chain termination by hydrolysis and achieve sufficient molecular weight which are typically in the range of 10,000-50,000 Dalton. [38] One concern of using the acid chloride route is the byproduct hydrogen chloride present. In electrical insulation, chloride ions are notorious for copper surface modification, leading to poor adhesion between the polymer and copper metal. To overcome these drawbacks, the diisocyanate route was then developed and also used for the PAI syntheses present in this work.

b) Diisocyanate route

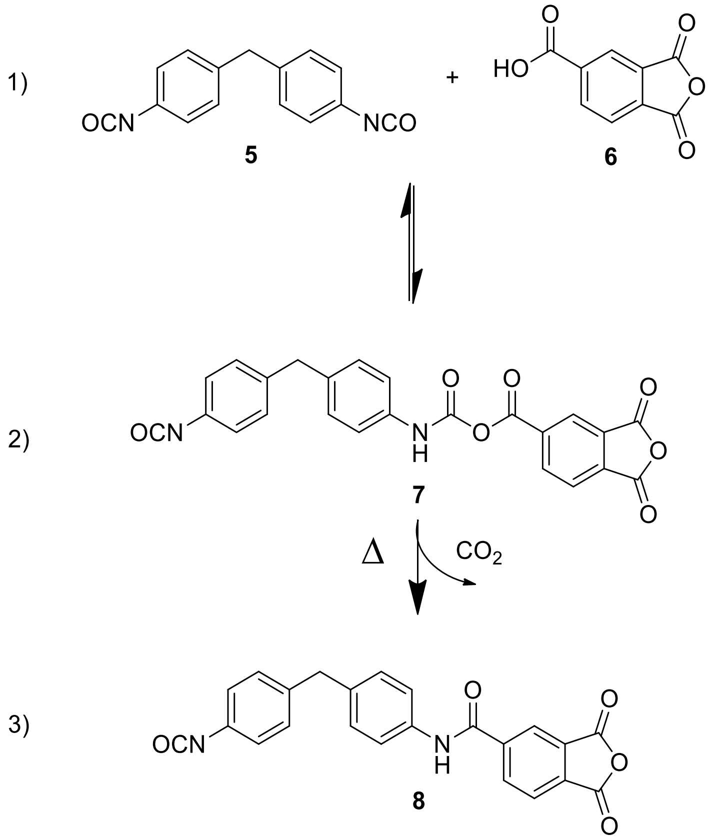
The diisocyanate route used in this study based on the work of Hitachi Chemical Corp. and nowadays is the most common for preparation of PAI resins for wire enamels.[39]

The isocyanate route comprises the condensation of an aromatic diisocyanate as 4,4′-methylenediphenyldiisocyanate (MDI) with aromatic tricarboxylic acid anhydride as trimellitic anhydride to give PAI without undergoing the polyamic intermediate since CO_2 is easily removed (Scheme 2).[40-44]



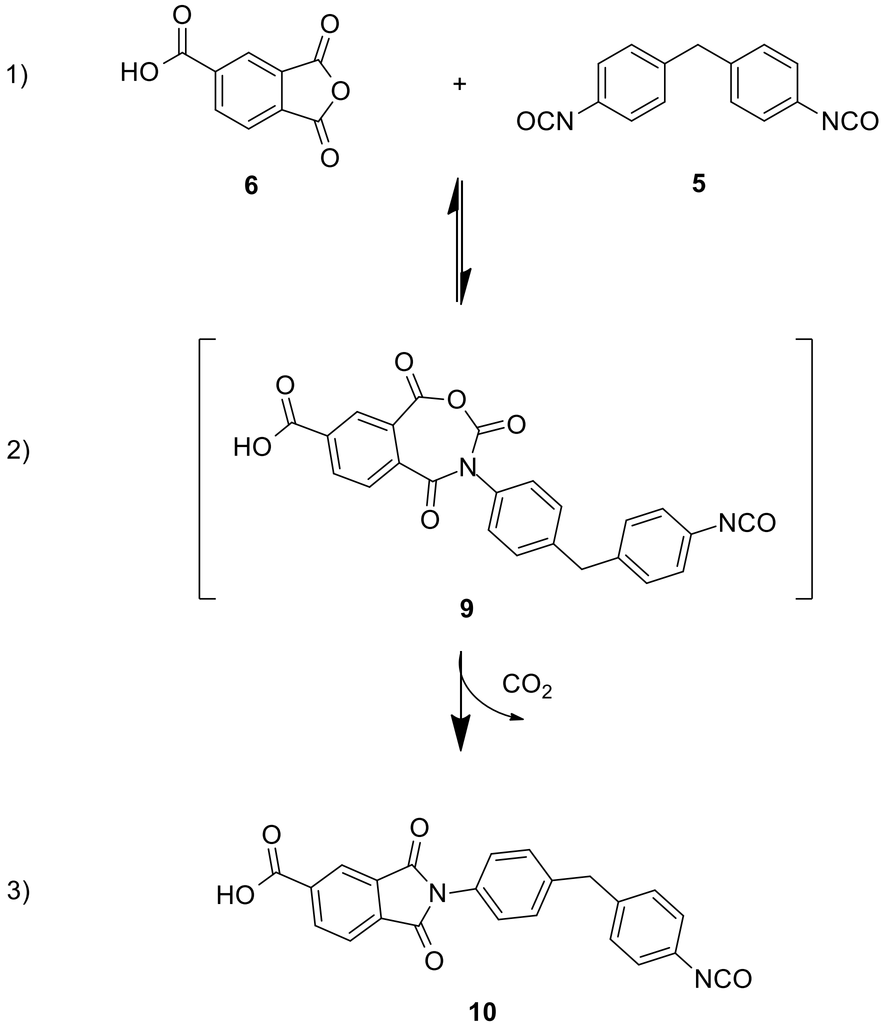
Scheme 2. Diisocyanate route.

A reaction scheme of amide formation is shown in Scheme 3. The monoacid functionality of TMA reacts directly with the isocyanate functionality (Scheme 3.1) to give the mixed anhydride intermediate **7**, *N*-carboxyanhydride (Scheme 3.2). In the last step, amide group is formed by decarboxylation of the mixed anhydride with release of carbon dioxide (Scheme 3.3). [45-46]



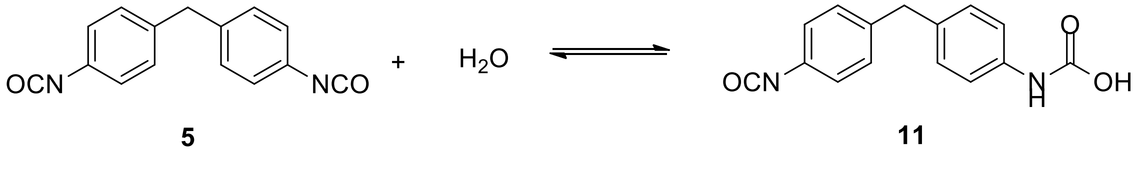
Scheme 3. Amide bond formation via reaction of TMA and MDI in (1) over N-carboxyanhydride (2) followed by decarboxylation to amide structure (3).

A reaction scheme of the imide formation is shown in Scheme 4. Formation of the imide bond takes place via a seven-membered rig intermediate **9** (Scheme 4.2) and subsequent decarboxylation with ring closure (Scheme 4.3). [47-50] It is of interest to note that the reaction occurs at low temperature. The formation of imide group is about 10 times faster than amide part due to higher reactivity of the anhydride ring. [51-53]



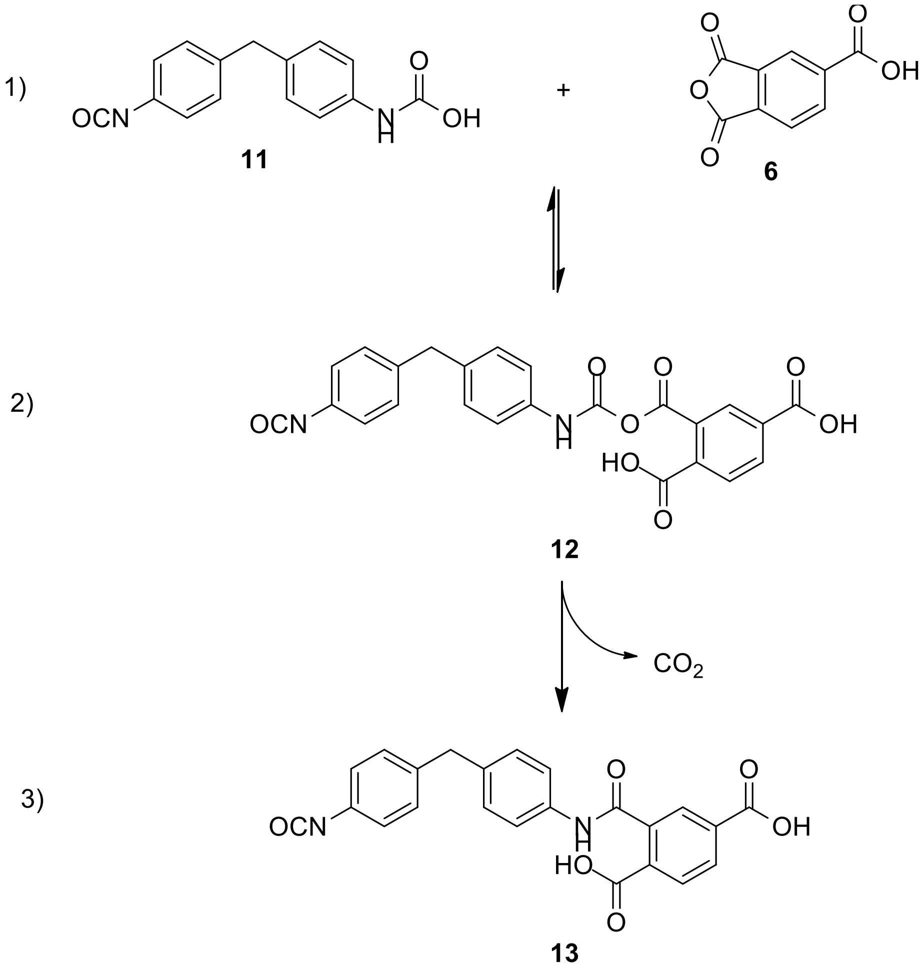
Scheme 4. Imide bond formation: isocyanate and anhydride groups (1) react forming a seven-membered ring intermediate (2) and the subsequent decarboxylation forms the imide group (3).

In the literature is present another possible reaction mechanism for the formation of the imide bond via the diisocyanate route. It is thought that the reaction starts with the formation of the carbamic acid, catalyzed by a protic species; water, as a residual impurity in the solvent (Scheme 5).

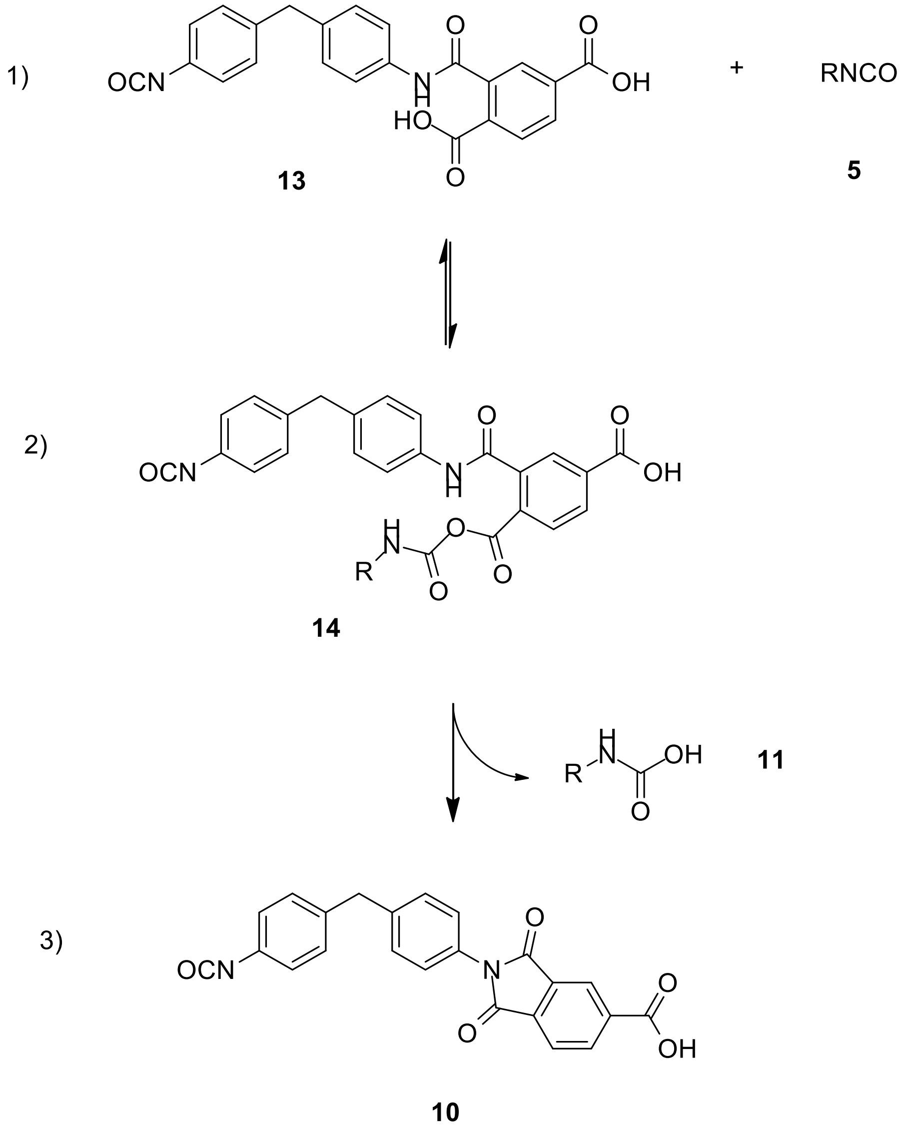


Scheme 5. Formation of carbamic acid.

Reaction of the carbamic acid with the anhydride forms the mixed anhydride of *n*-acetylated carbamic acid and a carboxylic acid (**12**) (Scheme 6.2). This mixed anhydride decarboxylates to form the amic acid **13**, releasing a molecule of CO_2 (Scheme 6.3).

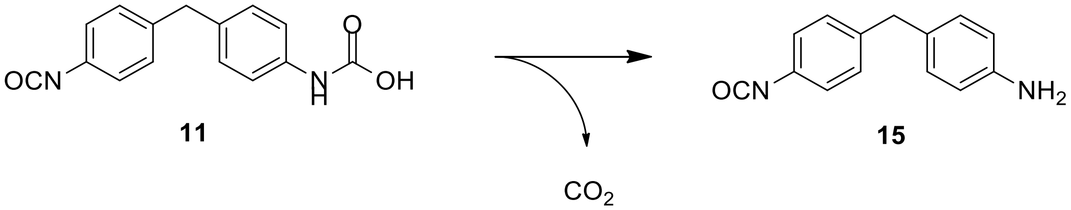


*Scheme 6. Formation of amic acid via decarboxylation of **12**.*



Scheme 7. Cyclization of imide ring.

The unstable carbamic acid is then free to react with another anhydride or to decompose to the amine with concomitant release of carbon dioxide (Fig. 12.8).



Scheme 8. Carbamic acid decomposes to amine and carbon dioxide.

In isocyanate chemistry many unintended side reactions can occur. The amine formed from the unstable carbamic acid can react with isocyanate, forming a urea. This secondary nitrogen urea or any other amide nitrogen may react further with another isocyanate, forming cross-link with the biuret functional group. The amine may also react with the anhydride of TMA, forming the amic acid. Depending on temperature, the isocyanate may react with the solvent itself and also with another isocyanate. All these side reactions and their influences on stoichiometry must be fully understood and controlled.[54-55]

The isocyanate route is performed at higher temperatures to evolve CO_2 gases and promote imidization reactions. The reaction temperature is ramped over time to promote all the various reactions shown above. A typical method starts the reaction at 80°C with the temperature increased at a rate of 30°C/h to 200°C over 4 h. Here the maximum CO_2 evolution occurs in the 120 to 130°C range, with no more evidence of isocyanate functional groups present. [56]

The polyamide-imide achieved at the end of this process is a solvent-based high molecular weight, fully imidized polyamide-imide with no condensation by-products since the carbon dioxide gas is easily removed. This convenient form makes it especially beneficial for the manufacturer where the primary end use is wire enamel or another coating application. The solution viscosity is thus controlled by stoichiometry, monofunctional reagents, and polymer solids. The typical polymer solids level is 35 to 45% and it may be diluted further by the supplier or customer with diluents.

The PAI resin is finally cured on copper wires by enameling ovens. This process allows total evaporation of the solvent and promotes a further increase in the molecular weight of the polymer. It is important to clarify that no cross-link reaction takes place at this stage since no reactive sites are present on chain backbones.

A typical FT-IR spectrum of a PAI enamel is shown in Figure 16.

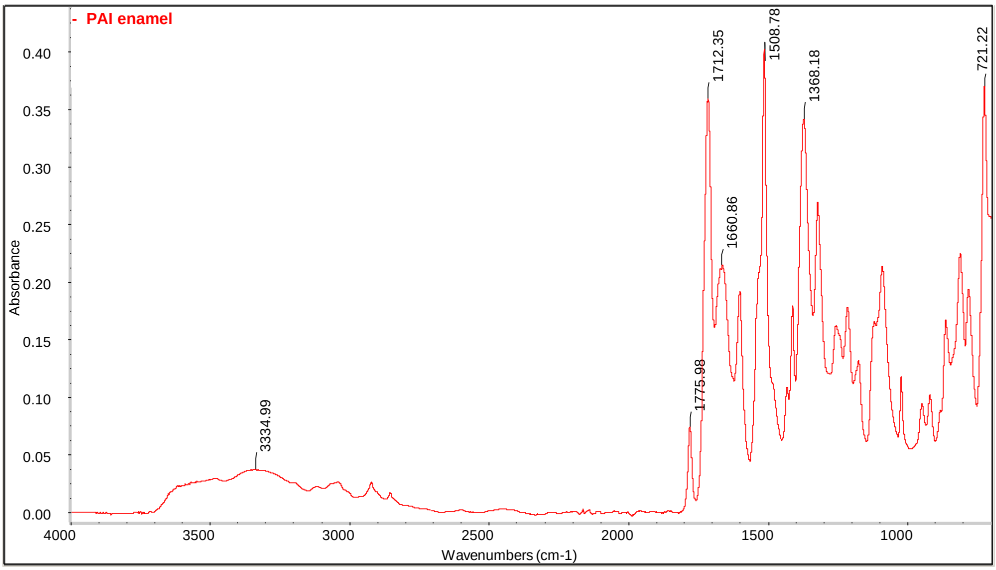


Figure 16. IR spectra of a typical PAI wire enamel.

Characteristic bands of a polyamide-imide are listed below:[57]

- Imide: symmetric and asymmetric stretching of C=O, respectively at 1715 and 1777 cm^{-1};
- Imide ring: stretching at 1371 and 720 cm^{-1}.
- Amide: stretching of C=O (amide I) located at 1665 cm^{-1}.
- Amide: bending of N-H (amide II) at 1510 cm^{-1}.
- Amide: stretching of N-H at 3401 cm^{-1}.

As inferred from the reaction schemes shown above, there is the potential for many side reactions. These complex reactions lead to a PAI with potential branch points and a slightly irregular polymer backbone compared to the acid chloride route. All the possible reactions are dependent on many parameters including the solvent, water content, monomer concentration, purity of reagents and temperature reaction profile. Because of the slightly irregular backbone and branching which reduce thermal stability, isocyanate-based PAIs are not seen in melt-processable PAI compounds. Another reason is that MDI is often the diisocyanate of choice. The methylene moiety is not stable at melt processing temperatures, leading to cross-linked material which does not flow well. In the acid chloride case, other diamines without methylene carbons, such as oxydianiline (ODA), are used for the injection-molding grades.

Variations to the diisocyanate route include the use of blocking agents during the synthesis. Blocking agents such as phenol, chlorophenol and other hydroxyl components have been studied. The isocyanate group is reformed upon thermal reversion of the carbamate group upon heating. The isocyanate group can then react with TMA to form the amide-imide polymer. The blocking is believed to allow better reaction control by moderating the impact of exothermic reaction between isocyanate and acid groups.[58]

The solution viscosity is controlled by stoichiometry, monofunctional reagents, and polymer solids. The typical resin solid content level is 35-45% and it may be diluted further by the supplier or user with diluents.

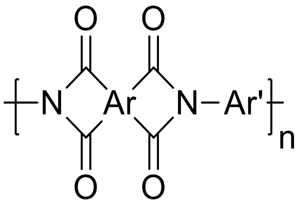
2.1.2. Polyimide

2.1.2.1. Properties and applications

Polyimides (PIs) are high temperature engineering polymers originally developed and commercialized by the DuPont Company in the 60’s and is known by the trade name Kapton™.[7,59] Polyimides are known for their capability of forming intra- and interchain electronic interactions called charge-transfer complexes (CTC), which are the reason behind their high thermo-mechanical properties and deep coloration.[60] In addition, due to the presence of the cyclic imide group and the polymer alignment from one chain and another, aromatic PIs exhibit an exceptional combination of thermal stability (> 500°C), mechanical toughness, and chemical resistance. They have excellent dielectric properties and inherently low coefficient of thermal expansion. Thanks to their versatility and characteristics, PIs have found diverse applications in microelectronics, flat panel display, aerospace, and chemical and environmental industries as flexible circuitry carriers, stress buffers, interdielectric layers, passivation layers, liquid crystal alignment layers, wire enamels, fibers, matrix materials, and gas and chemical separation membranes.[61-65] In the field of electrical insulation, cut-through temperatures of more than 500°C, high elasticity, not flammable and temperature indices of more than 240°C make PI wire enamels important materials for military purposes and space craft industry.[66-67] In the wire enamels sector, polyimides represent the polymers with the highest thermal class on the market.

2.1.2.2. Synthetic routes

PIs are characterized by the presence of the cyclic imide and aromatic groups in the main chains (Scheme 9).

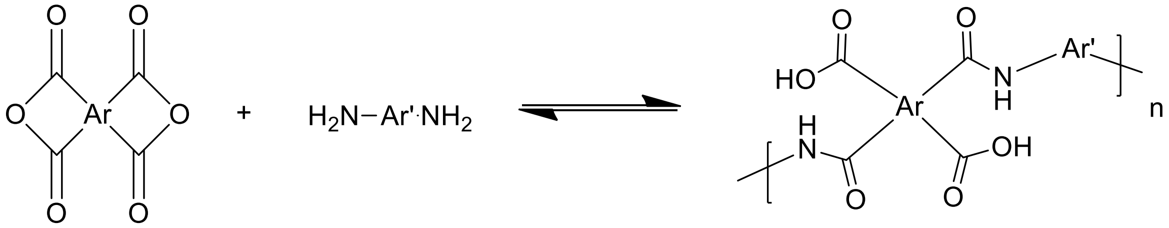


Scheme 9. Generic aromatic polyimide structure.

Several different synthetic routes have been developed over the years, and a large variety of materials have been prepared. In the field of wire enamel, a direct synthesis of high molecular weight aromatic polyimides in a one-step polymerization could not be accomplished because polyimides are usually insoluble and intractable in any solvent. For this reason polyimides are synthesized following a standard approach which involves polycondensation of pyromellitic dianhydride with an aromatic diamine such as 4,4'-oxydianiline, in two steps. The first step is polyamic-acid (PAA) synthesis (**a**) through exothermic polycondensation reaction in a polar aprotic solvent. The second step is solvent elimination and thermal imidization (**b**) of PAA to form the polyimide insulating coating. This approach has been faced and fully investigated.[68-69]

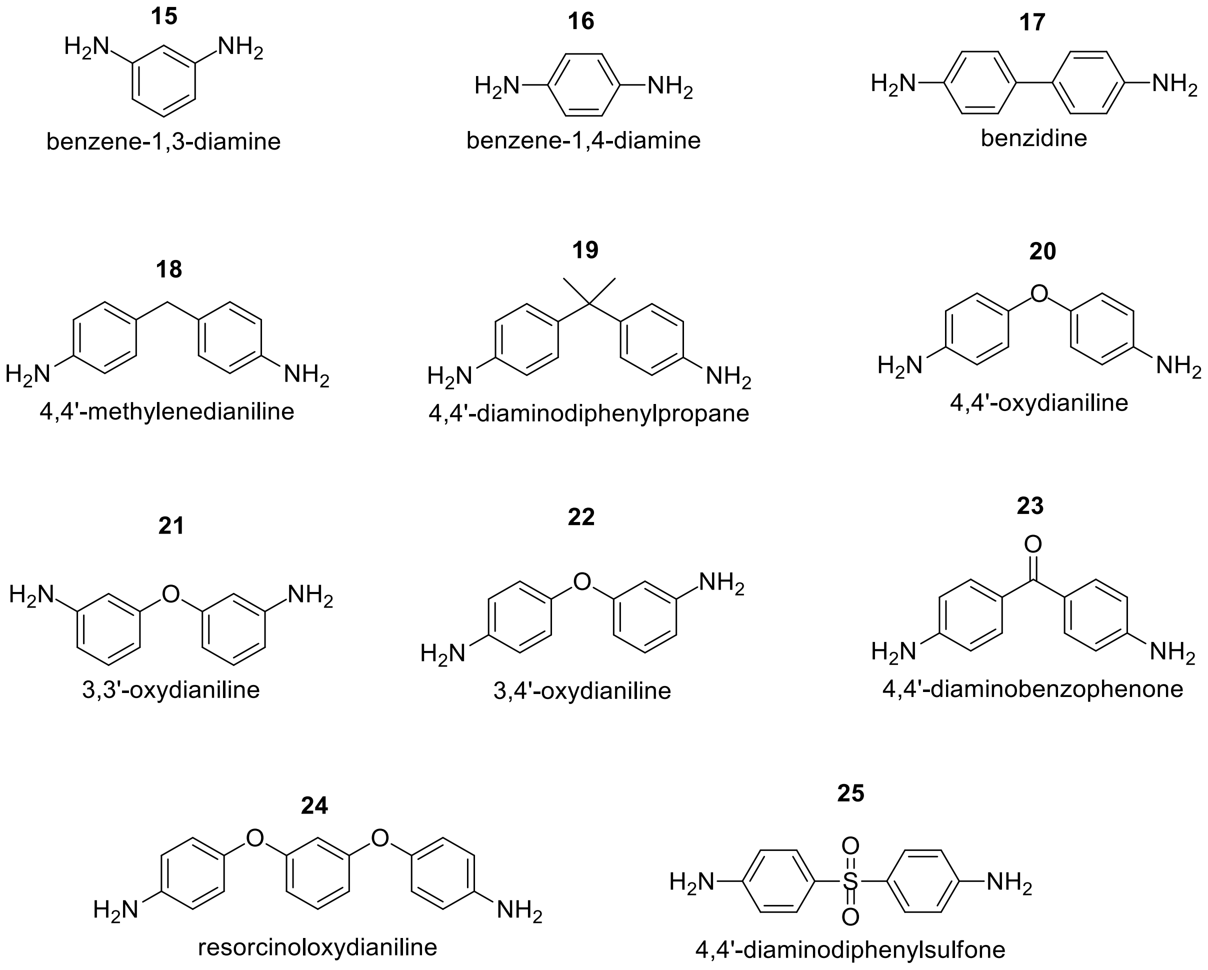
a) Polyamic-acid formation step

The first step involves the polymerization between the dianhydride and the diamine in a polar apolar solvent (as NMP, DMF, DMAc) at room temperature, giving a fusible polyimide precursor, known as polyamic-acid (PAA), in solution (Scheme 10).



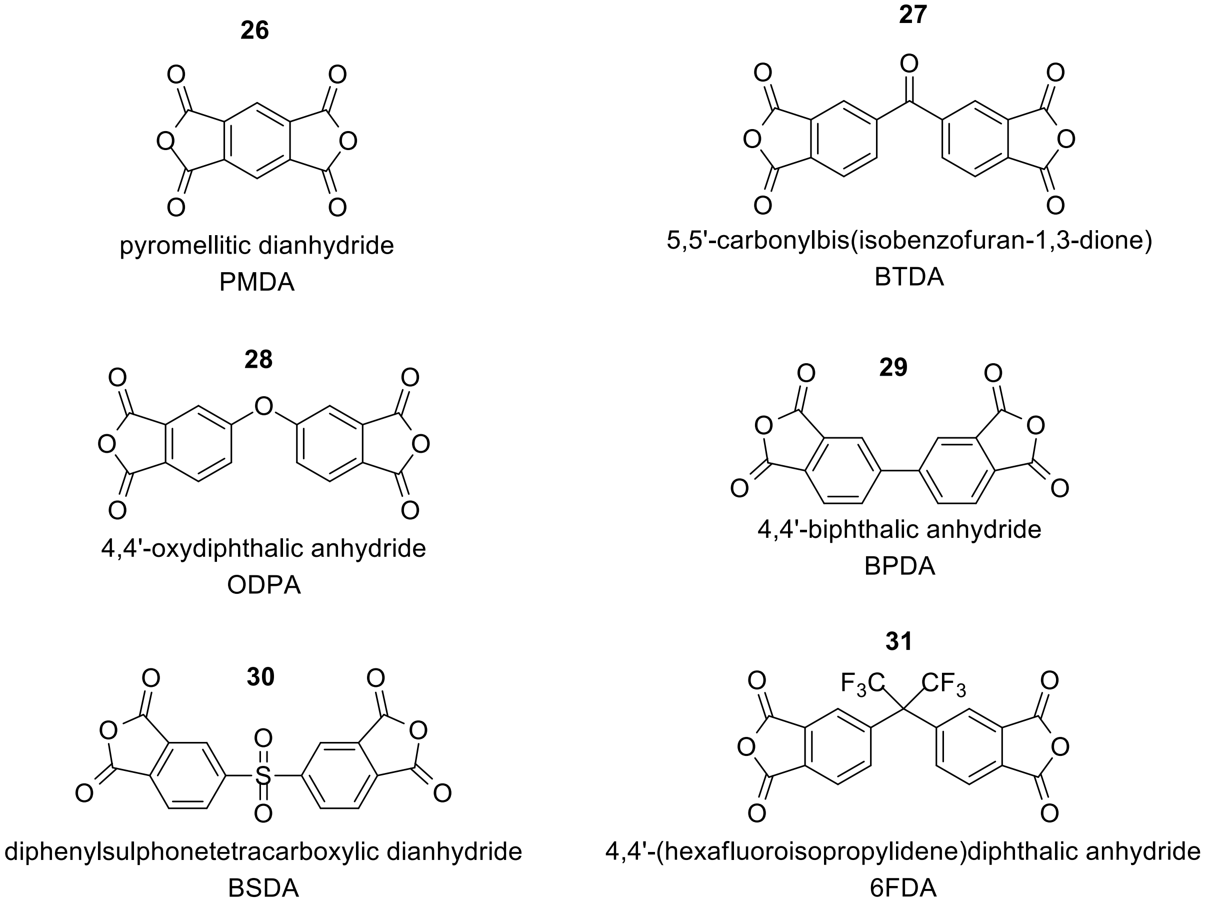
Scheme 10. Formation of the polyamic-acid.

Here most used diamines are reported (Scheme 11).



Scheme 11. Most used diamines.

Most used dianhydrides are reported here (Scheme 12).



Scheme 12. Most common dianhydrides.

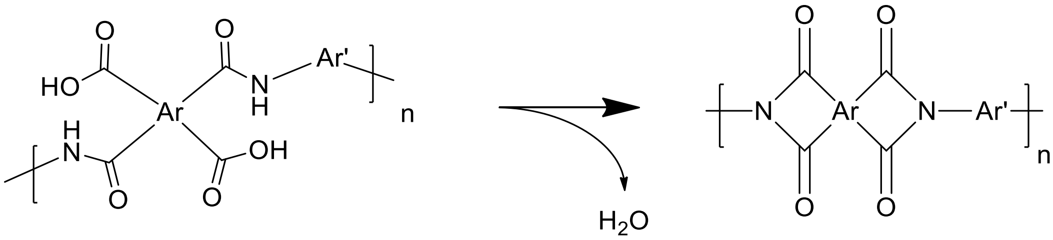
The forward reaction is thought to start with the formation of a charge transfer complex between the dianhydride and the diamine. Propagation occurs immediately thereafter via nucleophilic substitution at one of the anhydride's carbonyl carbon atoms. Thus, the amine nucleophile attacks the sp_2 carbon and displaces the adjacent carboxylate moiety. This results in a very unusual situation where the condensation by-product, the carboxyl group, is chemically attached to the product and the reaction is not driven to completion. For this reason, the important point to note is that the reactants and the product are in equilibrium, i.e., the propagation reaction is reversible.[70-71] Since PAA are synthesized with an equilibrium reaction, purity of the monomers is crucial to obtain high molecular weight PAA.

Another important observation to be made concerning the equilibrium is that the forward reaction is exothermic at ambient temperature.[72] The magnitude of the heat of reaction depends on the solvent's basicity. Thus, the equilibrium is shifted to the left and the product's molecular weight is lowered when the reaction temperature is increased.[73] Contrarily, lowering the reaction temperature shifts the equilibrium to the right and increases the molecular weight. In basic aprotic solvents, however, the equilibrium lies already so far to the right, at ambient temperature, that the increase upon cooling is usually not detectable.

Once produced, such viscous solutions are then commercialized and used to cast films or coatings.

b) Imidization step

In the second step, polyamic-acid is cured heating it to temperatures above 300°C: water is released, resulting in ring closure and imidization along the chain and formation of insoluble, infusible and heat resistant polyimides (Scheme 13).[74] Cyclodehydration to polyimide, can also be induced chemically by using dehydrating systems such as acetic anhydride and a tertiary amine at room temperature followed by a heat treatment for few minutes at 250 – 300°C.[75]



Scheme 13. Imidization of the polyamic-acid.

This is usually performed by a processing operation, whereby a polyamic-acid solution is used to cast a film, form a coating, or spin a fiber. Molding powders are also prepared by the precipitation of polyamic-acids from various solutions.[76-78] In wire enamels, PAA is applied and thermally cured to PI on copper or aluminum wires by the enameling oven at around 500°C. Polyimide films based on PMDA-ODA are a yellow, transparent material and have a modulus of 3 GPa and a tensile strength of 170 MPa. Those films cured at 400° C have no definable glass transition temperature below 400° C and exhibit less than 1.5% weight loss up to 500° C under nitrogen.[76] The material rapidly degrades at this temperature if exposed to air. This polyimide is insoluble even in highly polar solvents and processing must be accomplished during the polyamic-acid stage. Premature imidization of the polyamic-acid will form precipitates in the reaction mixture and for this reason, the first step has to be conducted at low temperatures (< 70°C). By varying the structure of the diamine or dianhydride polyimides of varying properties may be synthesized. If less rigid or flexible chemical spacer units are incorporated into the structure, soluble polyimides may be prepared.[79]

Solvent-based polyamic-acids exhibit higher viscosity compared to other polymers due to their high degree of polymerization and, in order to have a good processability, they must be diluted more.

IR spectroscopy highlights the characteristic bands of a polyamic-acid and its imidized form after the curing step (Figure 17).

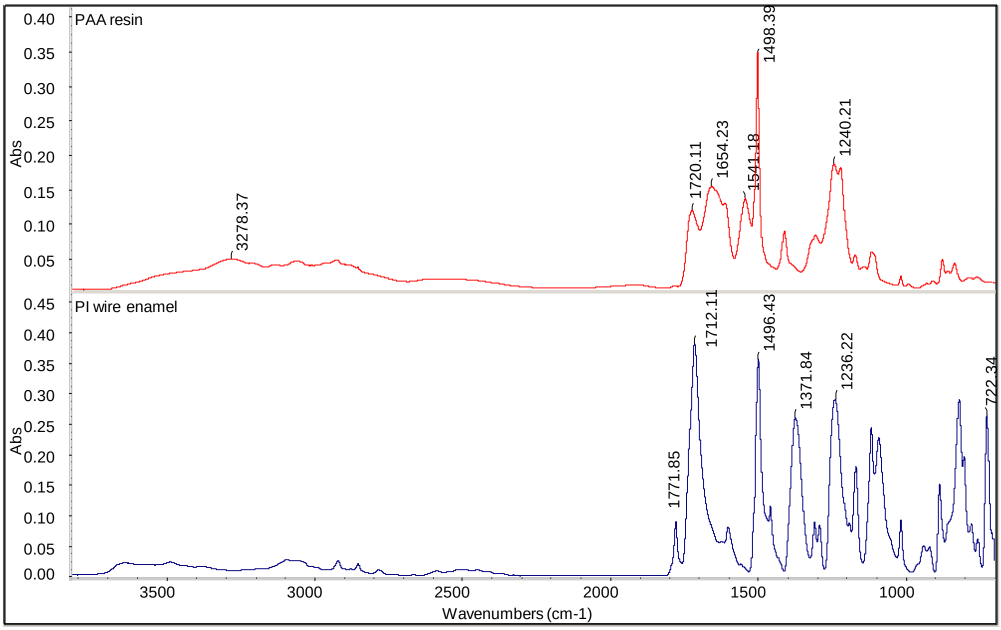


Figure 17. Top: FT-IR spectra of PAA resin before the curing step. Bottom: PI enamel after the curing step.

It is noticeable that differences are evident. The FT-IR spectrum of the PAA (top) shows broad bands in the range of 3500–2500 cm^{-1} which indicates the existence of –COOH and –NHCO– groups in the PAA. The peak at 1720 cm^{-1} (C=O stretching vibration) is representative of a C=O structure. The apparent peak at 1541 cm^{-1} is related to the amide II peak present in the backbone of the PAA polymer, which corresponds to the combination band of the N–H bending and C–N stretching vibrations (as seen in PAIs). The N-H bending of amide II (as seen for PAIs) and the peak around 1240 cm^{-1} indicates the existence of C–N bonds. FT-IR spectrum of the thermal-imidized PI (bottom) presents imide carbonyl peaks at around 1772 and 1712 cm^{-1}, and does not present any amide carbonyl peaks at 1654 and 1541 cm^{-1}. Other characteristic absorption bands of the imide group are observed at 1372, 1236, and 722 cm^{-1}. The narrow band at 1498 cm^{-1} is characteristic of the aromatic C=C absorption of the diamine, present in both spectra.

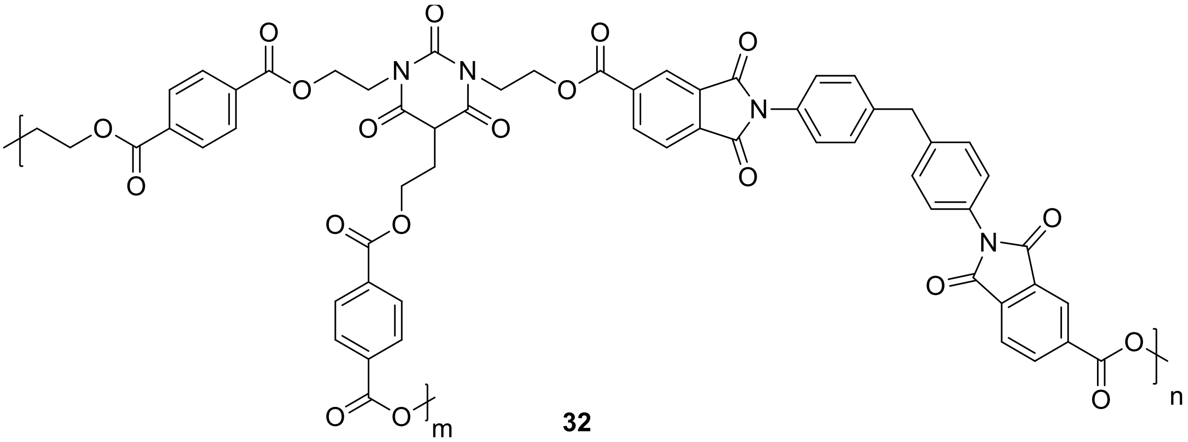
Although IR spectroscopy has been used extensively to monitor the cyclisation step, there is little agreement on its sensitivity to the chemical changes taking place. In fact, there is no consensus on which of the various amide or imide bands should be followed. The bands which have been most widely used are imide absorptions near 1770 cm^{-1} (symmetrical stretch, C=O), 1370 cm^{-1} (C-N stretch) and 720 cm^{-1} (bending of C=O).[80] The degree of imidization is determined by comparing the intensities of these bands in a treated sample to those in a sample that is heated until no changes in the band intensities occur.[81-82] A study has also found that the 1770 cm^{-1} band and the band near 720 cm^{-1} are affected by anhydride absorptions that appear during the thermal cycle. This interference can result in significant errors in determining the degree of cyclisation, particularly when the 1780 cm^{-1} band is used.[83] The imide band near 1370 cm^{-1} , however, does not appear to be affected by any other absorbance.

2.1.3. Polyester-imide

2.1.3.1. Properties and applications

Polyester-imides (PEI) were developed with the intent of merging the good mechanical properties of terephthalic acid polyesters, used as copper wire coatings since the 1950s, with the excellent thermal resistance of polyimides, avoiding the processing limitations and the low storage stability connected with the latter.[84]

Polyester-imides were developed for the first time in the early 1960s by Dr. Beck and Co. GmbH.[4] At the same time, a particular branching agent was introduced by Schenectady, which could further improve the mechanical and thermal properties (above all cut through, temperature index and tan d steep rise) of the resulting polymer: tris(2-hydroxyethyl) isocyanurate (THEIC)). The new generation of THEIC-modified polyester-imides was born which is still nowadays the top performing version of commercially available polyester-imides (Scheme 14).[9] These characteristics make PEIs one of the most important wire enamel, and are used in practically all electrical equipment for the insulation of conductors and influencing the whole insulating system of a winding.[85]



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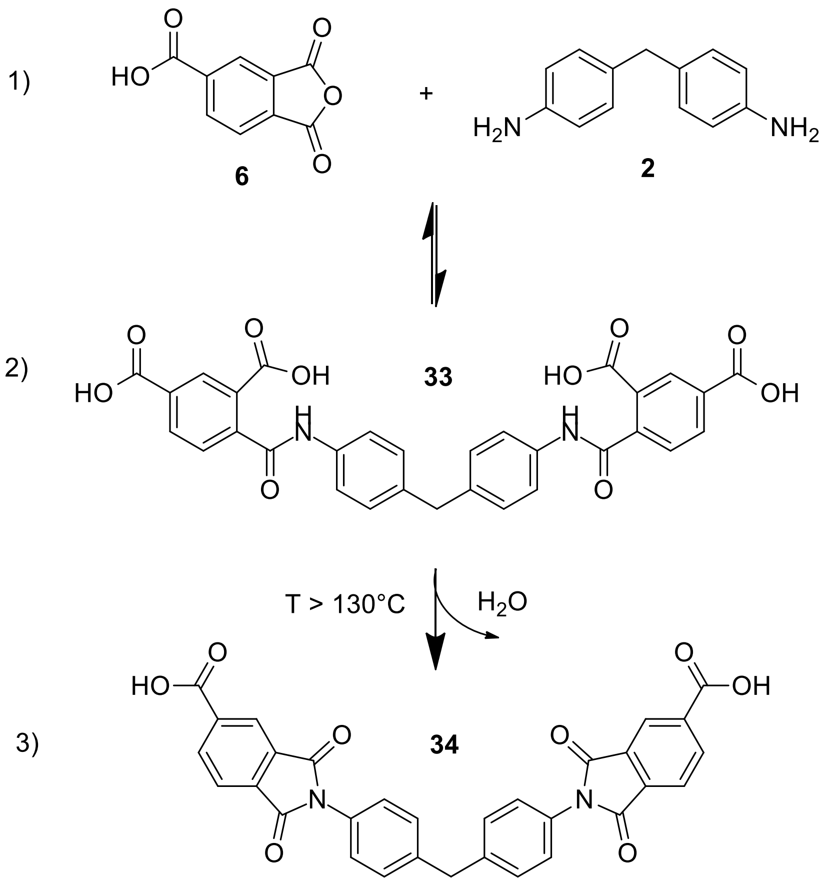
Scheme 14. Chain sequence of a THEIC-modified polyester-imide.

2.1.3.2. Synthetic routes

The synthesis of polyester-imide is based on the building of ester and imide groups that create the basic blocks of the polymeric structure.

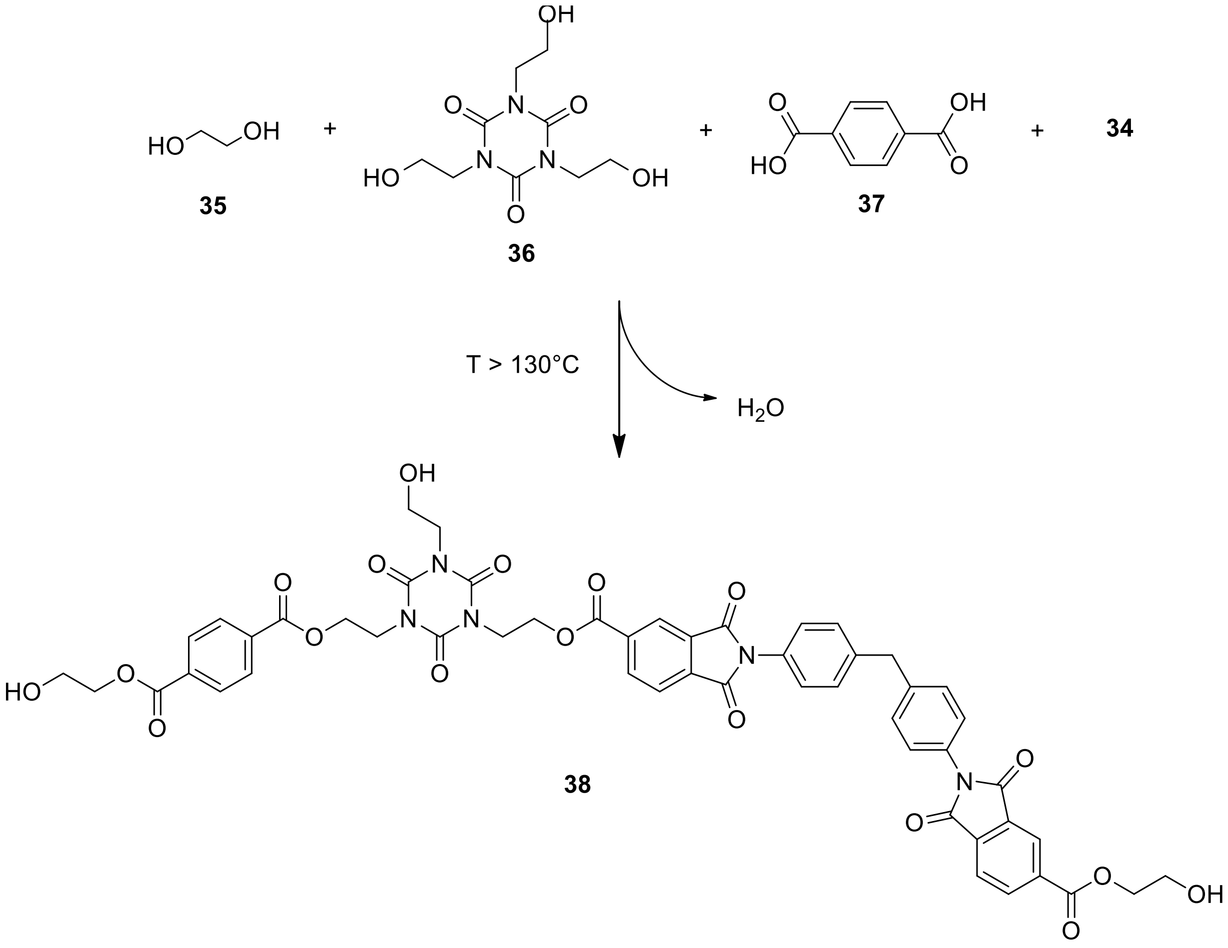
The first step involves the creation of an aromatic dicarboxylic acid with imide moieties by reacting two equivalents of an aromatic anhydride as trimellitic anhydride, with one equivalent of an aromatic diamine (Scheme 15). The most common diamine is 4,4'-methylendianiline (MDA) since aromatic diamines are today preferred to the previously used aliphatic ones like ethanolamine because they confer to the resulting polymer a higher resistance toward oxidative degradation and an improved hardness.[86-87]

Thanks to the different reactivity towards amines of the two functional groups (carboxylic and anhydride) belonging to the molecule, the formation of amic acid occurs preferably over amide formation (Scheme 15.2). Therefore, a diimide carboxylic diacid called DIDA **34** (Scheme 15.3) is formed after the ring closure of the amic acid with elimination of water. DIDA is an insoluble substance that becomes soluble in the polyester mixture once esterified, but there is a certain risk of creating a compact precipitate (called "cake") that could block the stirrer. Therefore, stirring, process temperatures, adding times and all process parameters must be accurately set and checked.



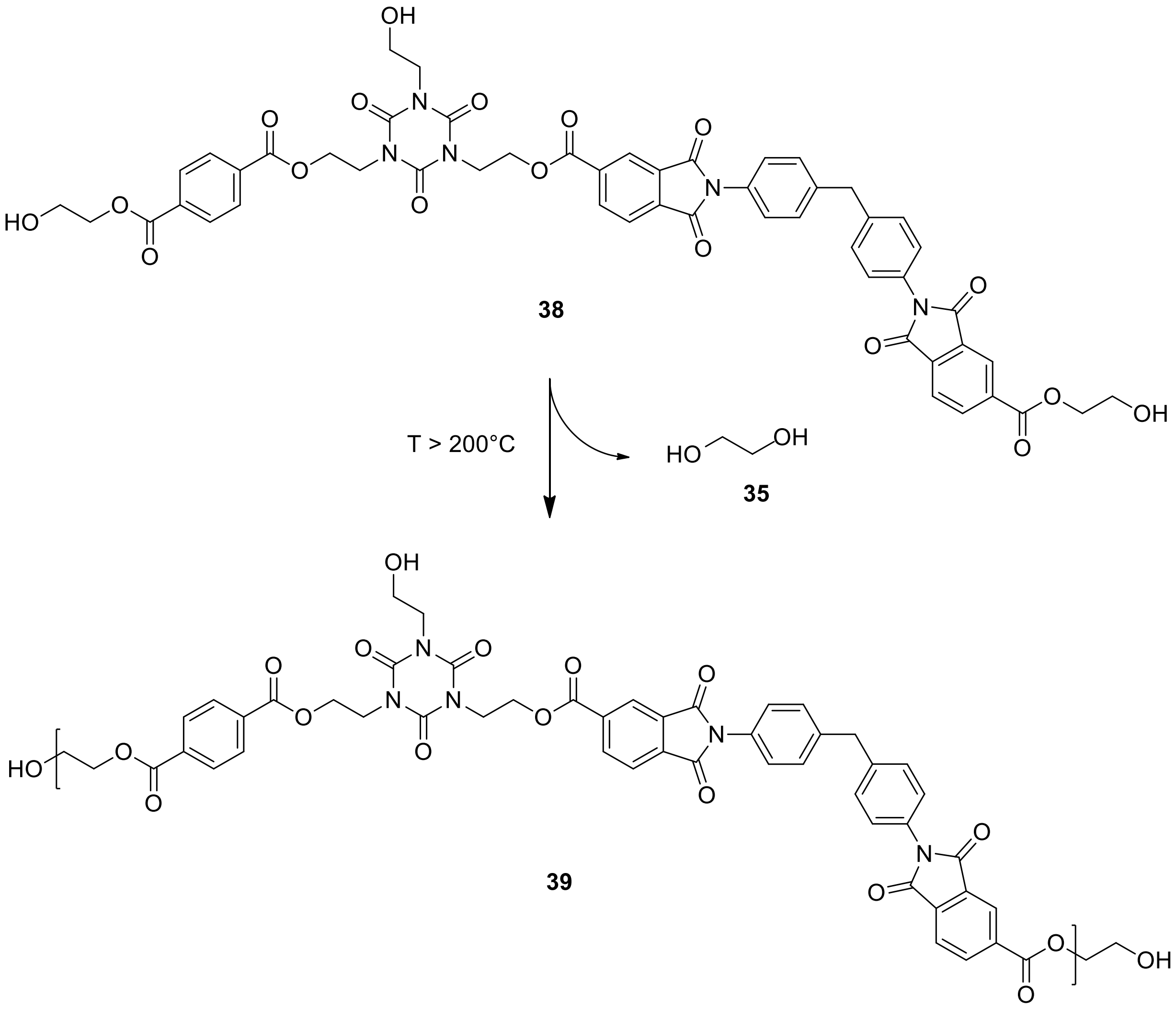
Scheme 15. Formation of DIDA.

At the same time, random esterification occurs between one equivalent of DIDA **34** and other carboxylic diacids as **37**, and an excess of di- and triols (**35**, **36**), producing low-molecular weight polyester oligomers (**38**) via polycondensation reaction with water elimination (Scheme 16). **38** has unreacted OHs functionalities due to the excess of di- and triols. All the DIDA has to be reacted, because the tiny needles of the acid left in the varnish would cause surface defects on the copper wire during the enameling process.



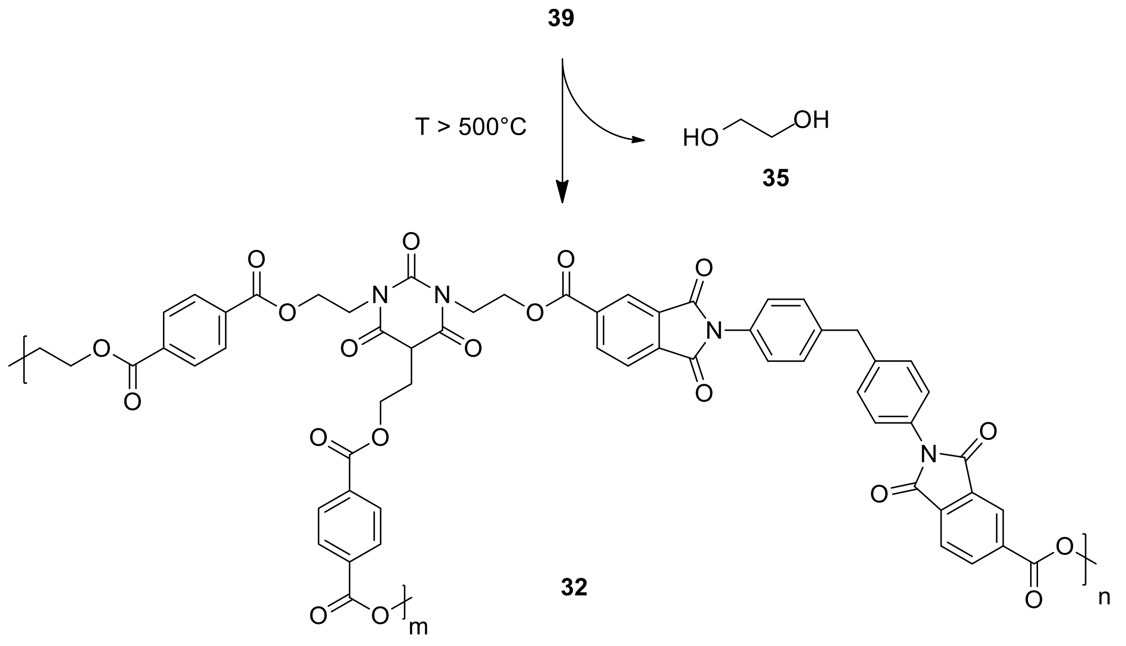
*Scheme 16. Esterification between **34**, **35**, **36** and **37**.*

Finally, transesterification occurs between terminal hydroxy groups of **38** through a polycondensation reaction with removal of glycol which is distilled off, giving **39** (Scheme 17). This process is fundamental to increase molecular weight of the polyester-imide. Excessive removal of ethylene glycol would result in gelling of the polymer due to cross-link reactions.



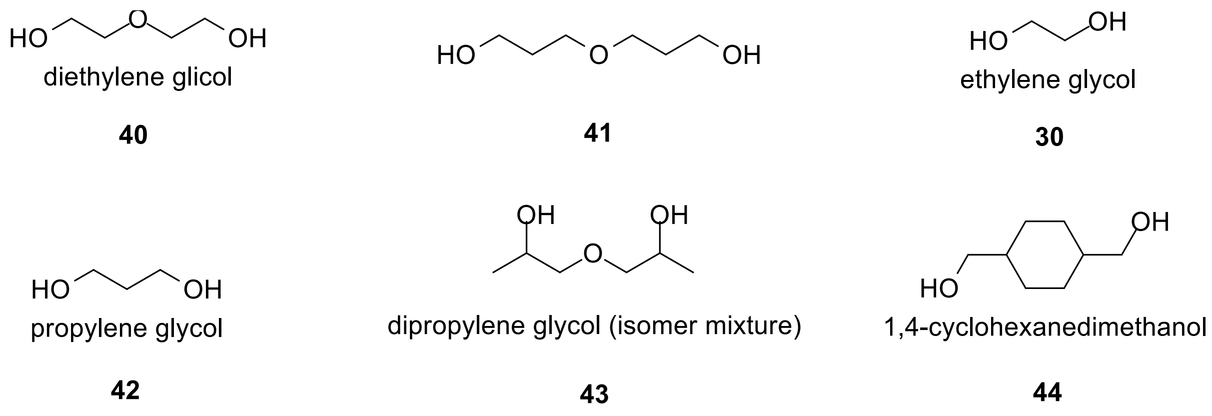
Scheme 17. Transesterification step.

Once the desired molecular weight is reached, the polymerization is stopped, and the resulting resin is applied on copper wires and cured. This process involves cross-link reaction between unreacted OHs.



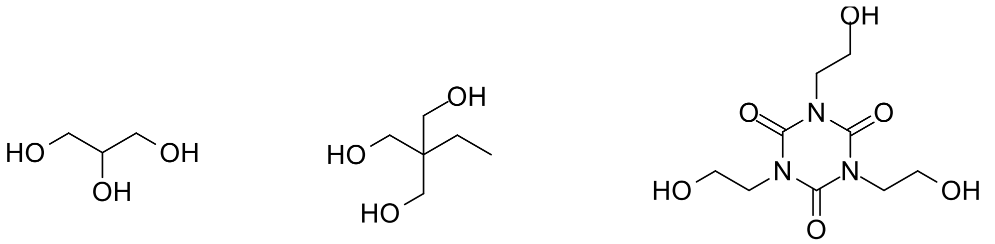
Esterification reactions can be catalyzed in many ways, e.g., by using metal (Mn, Sn, Zn, etc.) salts (acetates, octoates, etc.) or titanates, such as titanium butoxide monomer and titanium butoxide polymer (TBM and TBP) or titanium isopropoxide (TiPT). TBP is industrially preferred due to good quality of the resulting polymer (formation of side products is avoided) and a better waste management (no catalyst residue to be washed out, recovery of excess glycol in a relatively pure state).[88-90] The imide forming reaction needs no catalyst.

Many different monomers have been investigated over the years (especially in the 1970s) as possible reagents for the industrial synthesis of polyester-imides.[91-92] Among diols, the main ones used in the industry are ethylene glycol (EG), diethylene glycol (DEG), propylene glycol (PG), dipropylene glycol (DPG), 1,4-butane diol (BD), and 1,4-cyclohexanedimethanol (Scheme 18).



Scheme 18. Most used diols in PEIs.

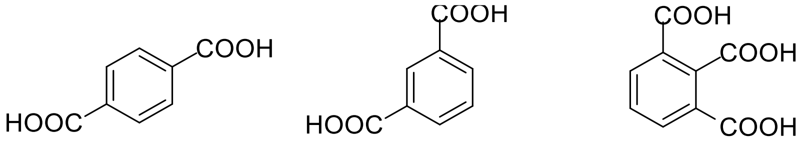
Thanks to its lower boiling point compared to other diols, MEG is preferred for its intrinsic capacity to be driven off during the transesterification step occurring in the oven application and easy removal from the coating film by diffusion and evaporation. Longer chain diols are mainly used to enhance polymer flexibility and resistance to breakdown.[93-94] Triols are introduced as branching agents used to increase thermal stability of cured enamels. Among them, most used are glycerin (gly), trimethylol propane (TMP) and tris(2-hydroxyethyl) isocyanurate (THEIC) (Scheme 19).



glycerine **45** trimethylolpropane **46** tris(2-hydroxyethyl) isocyanurate **36**

Scheme 19. Most used triols in PEIs.

When tris(2-hydroxyethyl) isocyanurate is used in PEIs, they are referred to as THEIC-modified PEIs. THEIC-modified polyester-imides are characterized by enhanced thermal properties like cut-through (roughly 30% higher compared to glycerin-based PEI), thermal index (+30%) and tan δ (+25%). Alternatively, it is possible to produce THEIC in situ via isocyanuric acid, although such a procedure leads to unwanted by-products that remain in the polymer, lowering general film characteristics. In the literature and in patents, several kinds of diacids supposed to confer various properties to derived PEI are reported.[95-98] Among the carboxylic diacid monomers usually used, the main ones are terephthalic acid (PTA), isophthalic acid (IPA) or trimellitic acid (Scheme 20).



terephthalic acid **37** isophthalic acid **47** trimellitic acid **48**

Scheme 20. Most used carboxylic diacids.

Reagents can be loaded in various ratios and at different reaction stages. Process conditions determine the resulting polymeric (or better oligomeric) mixture composition, which means that different conditions lead to different oligomer distributions. Even if the possibilities of monomers loading are wide, in industrial applications basically three main kinds of processes can usually be adopted.[99-104]

1) One step process: all components are charged one after the other, starting from polyols at room temperature, followed by the addition of the other components, while increasing the temperature.

2) Two step process: all components are charged in one step process, but partially. First, esterification or transesterification occurs with imide formation at high temperatures, then the mixture is cooled down and the remaining reagents are loaded for further reaction.

3) Two or more step process: in the first step, the polyols and the acid moiety are added with the catalyst, the esterification (or transesterification) takes place, then the diamine is slowly charged at relatively high temperatures and the imide group is allowed to form in the polyester mixture. Otherwise, TMA can be retained in the first step and added later, and the second addition can be split in two or more steps.

Industrial syntheses are performed in batches ranging from a few tons to tens of tons (according to reactor capacity). The reaction can be run in solvents like cresylic acids (mixtures of phenol, cresols, xylenols, ethylphenols, trimethylphenols, guaicols, anisols, and alkylated phenols in general) or in an excess of glycol, which is eventually removed during the condensation step.

To measure the polymerization grade, called also “condensation grade”, a simple method is to test the mixture viscosity, which grows proportionally to the molecular weight build, until the desired specification is reached. Alternatively, the growth of molecular weight can be directly measured by gel permeation chromatography (GPC). Thanks to this technique, it is possible to follow the polymerization process and the formation and consumption of oligomers in the polymeric mixture during the condensation step.

Once the desired molecular weight is reached, PEIs are characterized by infrared spectroscopy.

A typical FT-IR spectrum of a PEI resin and cured wire is shown in

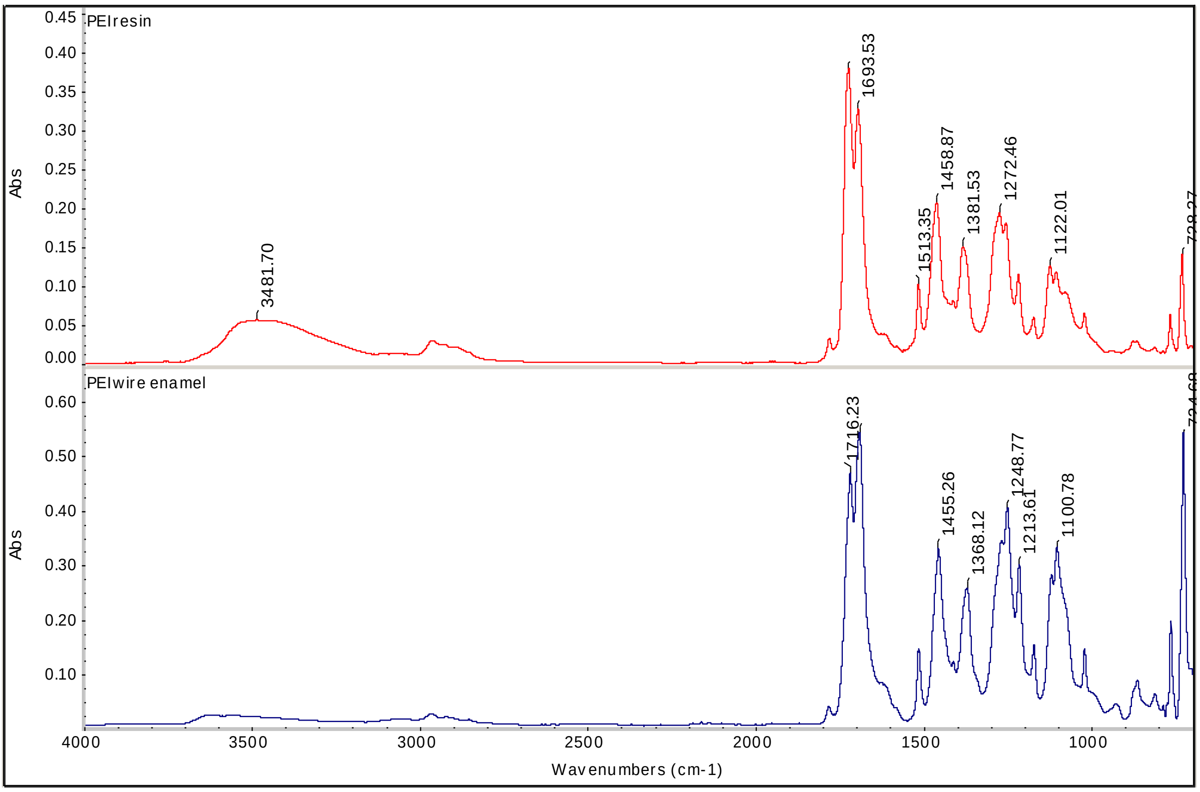


Figure 18. FT-IR spectra of uncured (top) and cured (bottom) THEIC-modified PEI.

From the uncured PEI FT-IR spectra, the band at around 3500 cm^{-1} is related to the hydroxyl and carboxyl groups. In the cured PEI spectra, characteristic main absorption bands of the carbonyl groups that are being part of either the imide ring, carboxylate groups and isocyanurate ring, occur in the spectral region between 1800 and 1600 cm^{-1}. In particular, the specific absorption peaks of the symmetric and asymmetric stretching of the carbonyl (C=O) of the imide ring are present at 1716 and 1775 cm^{-1}, while the stretching vibration of C=O on the ester bond appears at 1690 cm$^{−1}$.[105] The broad band relative to the -OH and -COOH groups it is almost gone in the cured sample. Absorption intensities vary according to the different raw material ratios.

PEIs are sold in mixtures of cresylic solvents and hydrocarbons. During wire oven curing, solvents and volatile monomers such as ethylene glycol, are removed, allowing the prepolymer to build molecular weight by transesterification to form a fully cured polymer. This reaction is catalyzed by titanium esters like butyl titanate.[106-107]

2.2. The Solvent System

Solvents are unavoidable in the formulations of wire enamels and more generally organic coatings as they impart the right viscosity necessary for the curing process that is the film formation step. The choice of the correct solvents in the right proportions is essential to produce a high-performance wire enamel which does not present any surface defect, in fact volatile components of the formulation affect popping, sagging, and levelling but also adhesion, corrosion protection, and exterior durability. In order to use them in the correct way it is necessary to understand what is meant by solvent and how many different kinds exist, another important thing to consider when talking about solvents and their selection is whether they are hazardous for human health and the environment.

Solvents can be divided in three main categories: weak hydrogen bonding, hydrogen-bond acceptor, and hydrogen-bond donor/acceptor.

a) Weak hydrogen-bonding solvents

They are petroleum-distillate mixtures of aliphatic and aromatic hydrocarbons, called naphthas. They vary in volatility and in aromatic content. Commercial aliphatic naphthas are blends of straight chain, branched chain, and alicyclic hydrocarbons with a rather low aromatic hydrocarbon content. An advantage of aliphatic naphthas is the low cost, especially in terms of volume, as their densities and price per unit of weight are low. Aromatic hydrocarbon solvents, on the other hand, are more expensive than aliphatic, but they dissolve a wider range of polymers.

b) Hydrogen-bond acceptor solvents

Oxygenated solvents, such as esters, ester ethers, and ketones, are hydrogen-bond acceptors. Ketones are generally less expensive than esters with similar evaporation rates but, in some cases, esters and ester ethers may be preferred over ketones due to their lower odors.

c) Hydrogen-bond donor/acceptor solvents

Among the oxygenated solvents there are those with active hydrogens that are strong hydrogen-bond donor/acceptors, that is the hydroxy compounds, both aliphatic and aromatic. The most widely used volatile alcohols are methyl, ethyl, isopropyl, *n*-butyl, *sec*-butyl, and isobutyl alcohols. Less volatile compounds used are phenol and alkylated phenols like cresols, xylenols, ethyl phenols, trimethylphenols. Then nitroparaffins, that are highly polar hydrogen–bond acceptor solvents. Thanks to their increased electrical conductivity, resulted from the high polarity, they can be exploited in the electrostatic spraying application.[22]

2.2.1. The choice of solvent

The choice of solvent is crucial because a good solvent must comply different characteristics:

- It must avoid side reaction with reactants.
- It must solubilize well the final polymer.
- It must be stable during shelf-life.
- It must not cause problems during application and curing.
- It has to be affordable.
- It must not be toxic.

An important factor to take into consideration is that the molecular weight of polymers plays an important role in their solubility. In a given solvent at a particular temperature, as molecular weight increases, the solubility of a polymer decreases. The same behavior is also noticed for the solubility of crosslinked polymers. As degree of crosslinking increases, since strongly crosslinked polymers inhibit the interaction between polymer chains and solvent molecules, preventing those polymer chains from being transported into solution.

2.2.1.1. Hansen Solubility Parameters

A possible help could derive from comparisons between Hansen solubility parameters. According to Charles M. Hansen, since there are three types of interactive forces between molecules, there should be three types of solubility parameters:

- Dispersion forces, $\boldsymbol{\delta_d}$
- Polar forces, $\boldsymbol{\delta_p}$
- Hydrogen bonds, $\boldsymbol{\delta_h}$

In this approach, solvents are located in the ‘‘Hansen space’’, a three-dimensional representation of dispersion (δd), polar (δp) and hydrogen bonding (δh) parameters. The closer two substances are in the Hansen space, the more likely they are to exhibit the same solubilizing properties. They are based on the idea that “like dissolves like” where one molecule is defined as being “like” another if it bonds to itself in a similar way.[108-110]

The total solubility parameter δ, was arbitrarily set equal to the square root of the sum of the squares of the partial solubility parameters.

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \tag{1}$$

For mixed solvents, it is possible to calculate a weighted average of the three partial solubility parameters.

$$\begin{aligned} \delta_{d(mix)} &= (\varphi\delta_d)_1 + (\varphi\delta_d)_2 + \cdots + (\varphi\delta_d)_n \\ \delta_{p(mix)} &= (\varphi\delta_p)_1 + (\varphi\delta_p)_2 + \cdots + (\varphi\delta_p)_n \\ \delta_{h(mix)} &= (\varphi\delta_h)_1 + (\varphi\delta_h)_2 + \cdots + (\varphi\delta_h)_n \end{aligned} \tag{2}$$

Three-dimensional solubility parameters can be determined or calculated by a variety of methods. One of these is the use of the HSPiP software, which its database contains solubility parameters of a wide range of solvents, chemicals and also polymers. Solubility parameters can also be predicted from the software by entering the Simplified Molecular Input Line Entry System (SMILE) of the desired substance.[111]

To determine if the parameters of two molecules (usually a solvent and a polymer) are within range, a value called interaction radius (R_0) is given to the substance being dissolved. This value determines the radius of the sphere in Hansen space and its center is the three Hansen parameters. To calculate the distance (R_a) between Hansen parameters in Hansen space the following formula is used:

$$(R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \tag{3}$$

Combining this with the interaction radius gives the relative energy difference (RED) of the system:

$$RED = R_a/R_0 \tag{4}$$

- When RED < 1: the molecules are alike and will dissolve.
- When RED = 1: the system will partially dissolve.
- When RED > 1: the system will not dissolve.

2.2.2. The solvent system in wire enamels

In the field of wire enamel, the solvent system consists of two components: one which is added at the beginning of the reaction to dissolve monomers and act as reaction medium (viz, solvents), and the other dilutes the resin (viz., thinners) modifying the boiling characteristics of the system and its viscosity.[112]

Reaction medium are high boiling point, highly polar aprotic solvents which are hydrogen–bond donors and acceptors like NMP, DMF, DMAc and DMSO.

Diluents are composed of medium boiling point solvents, that are aliphatic and aromatic hydrocarbons like naphthas and xylene, and high boiling point solvent. The term “naphtha” covers a category of chemicals derived from petroleum distillates and natural gas condensates characterized by specific distillation ranges, e.g., 160–180°C. These chemicals are clean and flammable by nature, and, as such, can be used for a variety of purposes. The chemical blend can be adjusted for use in any number of specific applications.[113] Among high boiling point solvents, the classical ones are phenol, cresols (a technical mixture of meta and para cresols), xylenols (mixtures of different isomers of dimethyl phenols), cresylic acids (mixtures of phenol, cresols, xylenols, ethylphenols, trimethylphenols, anisols, guaicols and alkylated phenols in general), and synthetic alkylated phenols. Distillation temperatures are in the range of 190–250°C.

Thinners are added for various reasons. First, they are added to decrease the viscosity of resins improving their processability and application to the wire. They are less expensive than highly aprotic solvents and are added to lower the final cost of the enamel. In addition, thinners evaporates more rapidly than NMP during the continuous application of wire enamels. This cools down the varnish mixture, preventing undesirable crusting at the surface of varnish pools which lead to blistering of the film. In fact, the selected varnish-solvents must provide the proper evaporation rates, satisfying the temperature profile of the curing oven employed and the enameling speed desired, giving regular and smooth films.

To ensure uniform evaporation during baking, prelaminar attempts are made to achieve as harmonious a course as possible of the evaporation behavior of the steadily changing azeotrope. Abrupt changes often cause surface defects in the cured enamel film. Examples of these surface defects are shown in the figures below (Figure 19).

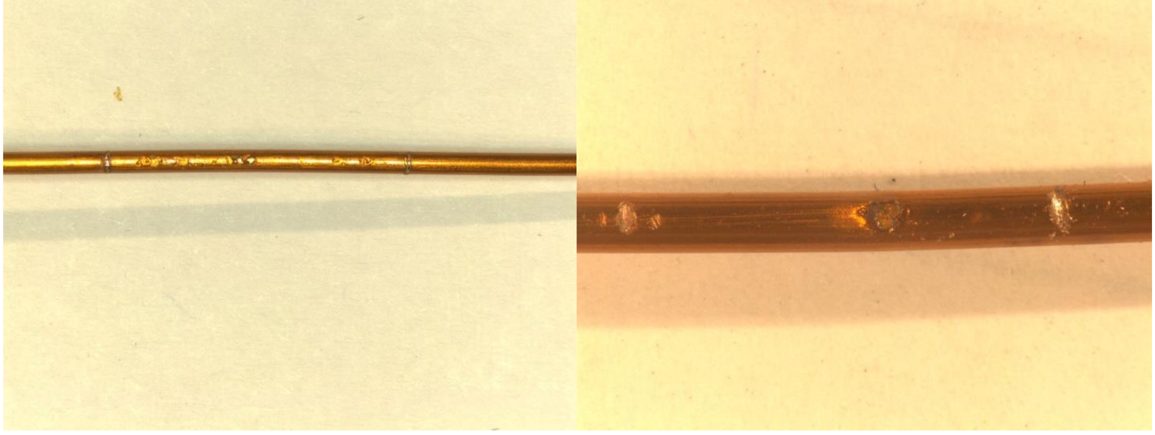


Figure 19. Blister formation on enameled wires. Note: from Elantas internal database.

As said before, solvents are crucial in the film formation step that occurs in the enameling ovens where these volatile components evaporate as the polymer is cured on the copper wire. For this reason, a more detailed treatment of the solvent evaporations rates is reported.

2.2.3. Evaporation Rates

Solvent evaporation rate is influenced by four variables: vapor pressure, temperature, surface to volume ratio, and rate of airflow over the surface.[114] The temperature to consider is that at and near the surface, the vapor pressure is that of the solvent at the temperature at which evaporation occurs. The ratio of surface area to volume is important because solvent evaporation occurs at the solvent–air interface, so if 10 g of solvent are spread out over an area of 100 cm^2, it evaporates more rapidly than if the surface area is 1 cm^2. As a result, the concentration of the resin solution and the viscosity increase more slowly during solvent evaporation from thicker films having the same surface area. Finally, the rate of airflow is considered because the evaporation rate depends on the partial pressure of the solvent vapor in the air at the air–solvent interface. If the vaporized solvent molecules are not carried away from the surface quickly, the partial pressure of the solvent builds up and evaporation is suppressed. Airflow rates vary substantially, depending on the application method and, therefore, the solvents used in a coating must be selected carefully for particular application conditions.[115-116]

Speaking of solvent selection, the most important variable to consider is the vapor pressure. A common error is to assume that boiling points (the temperatures at which solvents have a vapor pressure of 1 atm) are proportional to vapor pressures at other temperatures and so this parameter is used instead. However, boiling points are poor indicators of vapor pressure, and the two values can be very different for the same solvent, and it is difficult to judge how much more rapidly one solvent will evaporate than another from vapor pressure data. For this reason, there was the need to determine the relative evaporation rates (Eq. 5).[117]

$$E = \frac{t_{90}(n - butyl\ acetate)}{t_{90}(test\ solvent)} \tag{5}$$

This equation is used to determine the relative evaporation rate of a solvent (E) compared to that of the *n*-butyl acetate. In the equation, t_{90} is the time taken for 90 wt% of a sample to evaporate in a given type of apparatus under controlled conditions. So, the higher the E value, the faster the evaporation rate. Relative evaporation rate is affected by a lot of parameters such as vapor pressure, temperature or surface area, given that the evaporation is a surface phenomenon. Determination of relative evaporation rates requires measurement under standardized conditions.[118]

By focusing on the coating film formation process, it is to be said that the resin components have little or no effect in the initial rate of solvent evaporation rate, however as the loss of solvent from a coating continues, it is achieved a stage in which the evaporation rate slows down steeply. At a certain point the viscosity of the coating increases, leading to a decrease in the free volume available and the rate of loss of the solvent becomes dependent on the rate of diffusion of the same, rather than on the rate of evaporation.

Two phases of solvent evaporation can be identified. In the first stage the rate is governed by the factors that govern evaporation of the solvent mixtures. After a transitional stage, evaporation slows down, and the rate of solvent loss becomes dependent on the rate of diffusion of the solvent molecules through the film. During the second stage, diffusion rate is primarily controlled by free volume availability. That is, the solvent molecules move through the film by jumping from one free volume hole to another. The most important factor controlling free volume availability is (T-T_g). If solvent evaporation is occurring at a temperature well above the T_g of the solvent-free resin, diffusion rate will not limit the evaporation rate of the solvent at any stage of drying. As the T_g of the resin approaches the temperature at which drying occurs, evaporation of the solvent will become increasingly controlled by the diffusion rate as (T-T_g) becomes smaller.[119]

2.3. Polymerization Processes

Here are presented the two major classes of polymerization processes that can be involved in organic coatings formation: chain-growth and step–growth polymerization.

Chain-growth is often called addition polymerization, but this terminology is inadequate. While all chain-growth polymerizations involve addition reactions, not all addition polymerizations involve chain-growth reactions. There are four principal mechanisms of chain growth polymerization: free radical, anionic, cationic, and coordination. Furthermore, in this chemical process three different types of reactions are always involved, initiation, propagation, and termination while a fourth one, chemical transfer, in some cases can be a significant side reaction that leads to the termination of one chain and to the formation of another free radical which may initiate a second chain.

Initiation occurs when an initiator reacts to form an initiating free radical which, in turn, adds rapidly to a monomer molecule to form a second free radical. The polymer chain grows by the propagation reaction, in which the monomer free radical adds to a second monomer molecule to extend the chain and form a new free radical, this is propagation, and it is very fast. At any moment, the concentrations of monomer and polymer greatly exceed the concentration of growing polymer molecules. The final stage is termination of the growing chain. Two common types of termination reactions are combination and disproportionation. In most free radical initiated polymerizations, the rate of propagation is faster than the rate of initiation, which is limited by the rate of formation of the first free radical.[120]

2.3.1. Step-Growth Polymerization

With regards to step-growth polymerization, this is the process that interests us the most since the majority of the polymers used as enamels for wire insulation follow this polymerization method, such as polyesters, polyamides and polyurethanes to name a few.

As the name suggests, step growth polymerization proceeds in a step wise fashion. The functional groups on two monomers react to form a dimer, the dimer reacts with another monomer to form a trimer, and these reactions lead to many monomeric units linked to form an intermediate molecular weight material, which is known as an oligomer, and eventually a polymer.[121-124] The steps involved in the formation of a polymer in step growth polymerization are schematized in Figure 20.

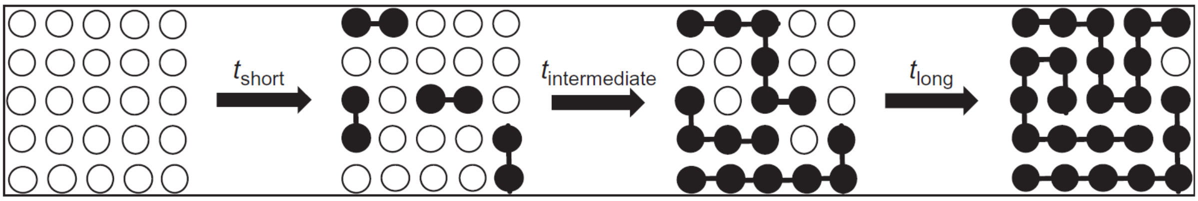


Figure 20. A generic representation of a step-growth polymerization. (Single white dots represent monomers and black chains represent oligomers and polymers). Note: from Cowie, J. M.; Arrighi, V. In Polymers: Chemistry and Physics of Modern Materials, 3rd ed.; CRC Press: Boca Raton, FL, 2008.

This means that high-molecular-weight polymers are formed after a large number of steps in which most monomers are consumed early in the polymerization to form short chains (oligomers) that combine to long polymer chains at a later stage of the polymerization. Due to the nature of this mechanism the reaction has to proceed for a long time to achieve high molecular weight polymers (Figure 21).[125-126]

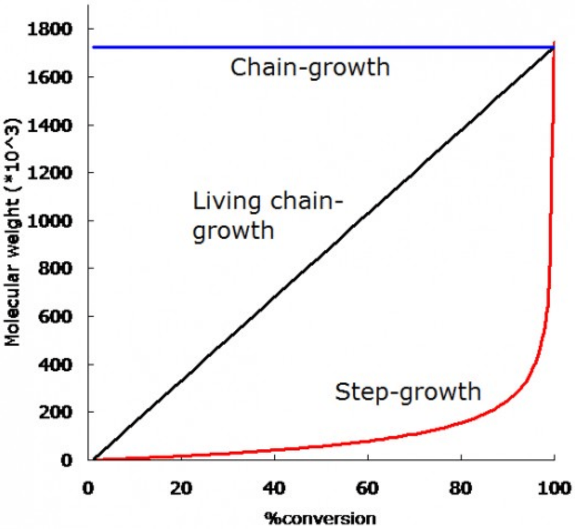


Figure 21. Polymer growth kinetic profiles for chain-growth, living chain-growth and step-growth polymerizations. Note: from https://polymerdatabase.com/.

In spite of this, step-growth polymerization offers several advantages over chain growth polymerization; for example, no initiator is required to start the polymerization and termination reactions are absent (Table 4).

Step-growth process can be divided into two classes: condensation and addition polymerization. In the case of condensation reaction, two monomers combine together with the loss of a small molecule, usually an alcohol, water or even carbon dioxide, while the addition reaction involves only the rearrangement of the electrons of a double bond to form a single bond with another molecule. An example of polycondensation is the reaction between ethylene glycol and terephthalic acid yielding a polyester while a typical step-growth polyaddition is the formation of a polyurethane by reacting a polyol with a diisocyanate.

It should be noted that if the monomers have functionalities higher than 2, not linear chains are obtained, but branched or crosslinked polymers instead, and the polymerization is referred to be polyfunctional step growth.

Table 4. Step-growth vs. chain-growth polymerization.

Step-Growth vs. Chain-Growth polymerization		
	Step-Growth	**Chain-Growth**
a) Reactions	One reaction is responsible for polymer formation.	Initiation, propagation, and termination reactions have different rates and mechanisms.
b) Polymer growth	Any two molecular species present can react; slow, random growth takes place.	The growth reaction takes place by the addition of one unit at a time to the active end of the polymer chain.
c) Polymer molecular weight	Molecular weight rises steadily throughout the reaction. High conversion is required for high molecular weight polymers.	High molecular weight polymer is formed immediately.
d) Monomer concentration during polymerization	Monomer disappears in the early stages of the polymerization. At an average degree of polymerization of 10, less than 1 weight percent of the monomer remains.	Monomer concentration decreases steadily throughout the reaction.
e) Composition of the polymerization reaction	A relatively broad, calculable distribution of molecular species are present throughout the course of the polymerization.	The mixture contains only monomer, high molecular weight polymer and only about 10^{-8} part of growing chains.

2.3.1.1. Molecular Weight Distribution in Step Growth Polymerization

The molecular weight distribution of a linear condensation or addition polymer can be easily calculated if it is assumed that each functional group has the same probability of reacting with other groups regardless of the oligomer size. This assumption is called *equal reactivity principle* by P. J. Flory. According to this principle, the probability that a given reactive group has reacted is equal to the fraction p of all condensed functional groups of the same type, which is called the extend of the reaction.[127] An oligomer containing x repeat units must have undergone x-1 reactions. The probability that this number of reactions has occurred is simply the product of all reaction probabilities, i.e., px^{-1}, where the probability of finding an unreacted end group is 1- p. Thus, the total probability, P_x that a given oligomer is composed of exactly x units is given by:

$$P_x = (1 - p)p^{x-1} \tag{6}$$

P_x is equal to the mole fraction, n_x, of x-mers in the reaction mixture of the extend p:

$$P_x = n_x = N_x/N \tag{7}$$

Then the total number of x-mers is given by:

$$N_x = N(1 - p)p^{x-1} \tag{8}$$

where N is the total number of molecules of all sizes. This number is related to the initial number of monomers or the total number of units, N_0, by:

$$N = N_0(1 - p) \tag{9}$$

where $DP = N_0/N$ is equal to the average degree of polymerization:

$$DP = N_0/N = 1/(1 - p) \tag{10}$$

With this substitution, the total number of x-mers can be written as:

$$N_x = N_0(1 - p)^2 p^{x-1} \tag{11}$$

If the weight of the condensing end groups of each molecule is neglected, the molecule weight of each molecule is directly proportional to the length of the chain x. Thus, the weight fraction w_x can be written as:

$$w_x = xN_x/N_0 \tag{12}$$

The error for condensation polymers will only be significant for low molecular weight polymers. Then, the weight-average molecular weight distribution is given by

$$w_x = x(1-p)^2 p^{x-1} \tag{13}$$

This distribution is called *Flory-Schulz distribution*. The form of this distribution implies that shorter polymer chains are favored over longer ones. It also implies that the length distribution widens and shifts to higher molecular weight with increasing extend of reaction. The weight fraction and mole distributions are shown in the figures below.

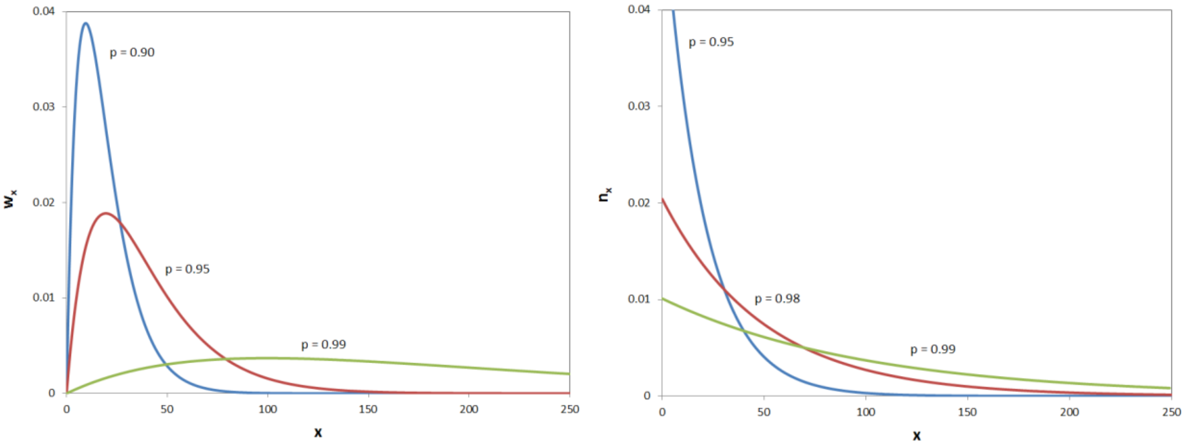


Figure 22. Weight fraction (left) and mole fraction (right) distributions of linear step-growth polymers. Note: from https://polymerdatabase.com/.

From the expressions above, the average molecular weight M_n can be easily calculated by:

$$M_n = mN_0/N = m/(1-p) \tag{14}$$

where m is the molecular weight of a repeating unit. The weight-average molecular weight M_w can be calculated as follows:

$$M_w = \sum_x w_x M_x = m(1-p)^2 \sum_x x^2 p^{x-1} = m(1+p)/(1-p) = (1+p) \tag{15}$$

where $M_x = x \cdot m$ is the molecular weight of a repeating unit.

An important parameter related to the average degree of polymerization is the ratio of weight and number average of the polymer molecular weight, M_w / M_n, and is called polydispersity (PDI) heterogeneity index D. It is a measure for the broadness of a molecular weight distribution. The polydispersity is unity if all polymer molecules are of the same size. The polydispersity for the most probable molecular weight distribution is given by:

$$D = m(1+p)(1-p)/[m(1-p)] = (1+p) \tag{16}$$

2.3.2. Molecular Weight Control

The molecular weight distribution of a polymer is one of the most important parameters because from it depends, to a large extent, the final mechanical and thermophysical properties such as glass transition temperature, viscosity and the mechanical strength, to name a few. A high molecular weight is often desired in many applications and, it can be obtained by step-growth only when three critical requirements are met: first, the two difunctional monomers (*A*-*A* and *B*-*B*) must be added at perfect stoichiometric ratio, i.e., the ratio of the concentrations of the reactive groups, *[A]/[B]*, must be equal to or very close to 1. In the case of a single bifunctional type *A*-*B* monomer such as amino acids or hydroxy acids, this balance is provided automatically. Secondly, the monomeric impurities that can react and terminate the gradual growth must be kept as low as possible because any trace of a monofunctional reactive compound will cap the growing polymer chains and thus reduce the molecular weight. However, rigorous purification of the reagents is often difficult and adds cost to the final product. Third, the step-growth polymerization must be driven close to completion in order to reach a very high yield and with no side reactions. In addition, the molecular weight must be about two times the entanglement weight which equals about 15 to 100 repeat units, depending on molecules structure.[128]

For these reasons, a relatively high conversion is required to achieve a high degree of polymerization. However, the true average degree of polymerization is often lower than the theoretical value. There are three main reasons for this discrepancy:

- some monomers may evaporate during the reaction;
- some monomers may undergo side reactions;
- monofunctional reactive compounds may be present in traces.

These events will lead to a stoichiometric ratio imbalance between monomer *A* and *B* with a consequent depression of the average molecular weight.

2.3.2.1. Stochiometric Imbalance of Bifunctional Monomers

Stoichiometric imbalance is defined by the ratio $N_{A,0}/N_{B,0}$, which cannot exceed unity by definition. Then the total number of reactive units is

$$(N_{A,0} + N_{B,0})/2 = N_{A,0}(1 + 1/r)/2 \tag{17}$$

where $N_{A,0}$ and $N_{B,0}$ are the total number of the monomers *A* and *B* that are present at the beginning. The number of unreacted *A* and *B* groups after the reaction has reached extent *p* is

$$N_{A,0} = (1 - p)N_{A,0} \tag{18}$$

$$N_{B,0} = (1 - pr)N_{B,0} = (1 - pr)N_{A,0}/r \tag{19}$$

and the total number of chain ends

$$(1 - p)N_{A,0} + (1 - pr)N_{A,0}/r = (1 - 2p + 1/r)N_{A,0} \tag{20}$$

which must equal to twice the total number of molecules since each molecule has two terminal functional groups. The numerical mean degree of DP polymerization is equal to the number of repeated units divided by the number of chains:[129-130]

$$DP = (1 + r)/(1 + r - 2pr) \tag{21}$$

At 100 % conversion ($p = 1$), this expression is reduced to

$$P = (1 + r)/(1 - r) \tag{22}$$

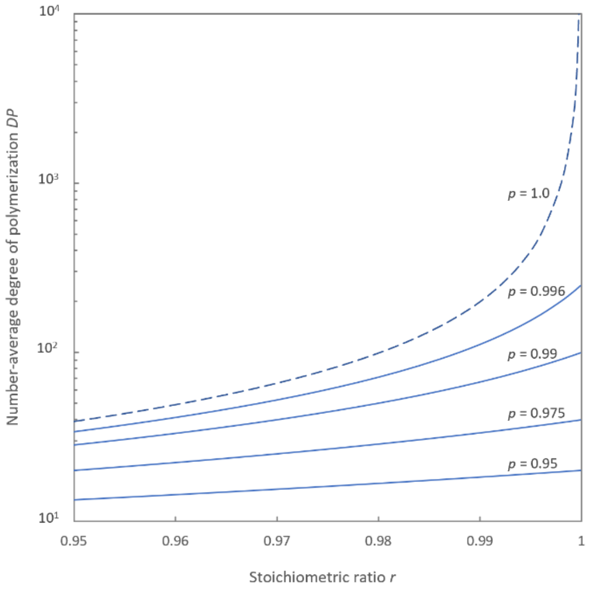


Figure 23. Number-average degree of polymerization as a function of the stoichiometric ratio. Note: from https://polymerdatabase.com/.

Figure 23 shows the effect of stoichiometric imbalance and conversion on the average degree of polymerization (*DP*). The latter drops as stoichiometric imbalance increases and conversion decreases. Thus, a small loss of reactant through evaporation of monomers or through side reactions can substantially limit the molecular weight of the final product. In addition, if the polymerization is performed to 99% completion instead of 100%, the degree of polymerization will reduce to 50 units. Therefore, to achieve a high *DP*, the reaction has to be driven close to completion.

2.3.2.2. The Role of Monofunctional Reactants

Adding a monofunctional reagent or an impurity to an equimolar mixture of *A-A* and *B-B*, will lower the molecular weight due to end-capping. The same equations can be applied to this situation if *r* is redefined as follows:

$$r = N_{A,0}/(N_{B,0} + 2N_{B,1}) = N_{A,0}/\left(N_{A,0} + 2N_{B,1}\right) \tag{23}$$

where $N_{B,1}$ is the initial number of the monofunctional *B* monomer. Factor 2 arises here because one molecule of *B* has the same quantitative effect in limiting the molecular weight as an excess of one *B-B* monomer. With this definition, the plots above describe the depression of the molecular weight induced by monofunctional monomers as well.

2.3.2.3. The Role of Trifunctional Reactants

Branched polymers can be formed when some of the monomers have 3 or more functional groups per molecule. However, the addition of trifunctional monomers can also generate cross-linked polymers. In other words, a step-growth polymerization involving trifunctional units can lead to the formation of insoluble cross-linked structures (gel fraction) embedded in linear and branched polymers (sol fraction) or to a one infinite insoluble polymer network.[131] The point in the polymerization where the polymer begins to form crosslinked structures (insoluble gel) is called the *gel point*. According to Flory, an infinite network becomes possible when at least one of the functional groups of the *f-1* branches has reacted with a functional group of another branch.[132] The probability α_c of this event is 1 in *f-1* or,

$$\alpha_c = 1/(f-1) \tag{24}$$

Hence, when trifunctional branch units are involved, infinite networks are possible only when $\alpha \geq 1/2$. The point at which the polymerization starts to form a crosslinked structure will depend on the degree of polymerization, the fraction of trifunctional monomers, and the stoichiometric ratio between *A* and *B*. According to Flory, the average degree of polymerization and the fraction of branched monomer units, can be calculated from:

$$DP = [f(1-\rho+1/r)+2\rho]/[f(1-\rho+1/r-2p_A)+2\rho] \tag{25}$$

$$\alpha = rp_A^2\rho/[1-rp_A^2(1-\rho)] = (p_B^2\rho)/[1-p_{BA}^2(1-\rho)] \tag{26}$$

where ρ is the ratio of *A* groups belonging to the branched molecules, to the total number of *A* groups, *r* is the stoichiometric ratio between *A* and *B*, and ρA is equal to the fraction of *A* that have reacted. Combining the latter expression with $\alpha_c = 1 / (1 - f)$, gives the following equation for the extent of reaction of *A* groups at the gel point:

$$p_c = 1/\{r[1+(f-2)]^{1/2}\} \tag{27}$$

For a reaction between a difunctional resin with a trifunctional resin, the critical branching coefficient is $\alpha_c = 0.5$ and the critical extend $pc = (0.5)^{0.5} = 0.707$ $(r = 1, p = 1)$. Hence, gelation occurs with a conversion of 70.7 %. In practice, gelation often occurs at higher values. This deviation has been attributed to the fact that functional groups on multifunctional monomers can have different reactivities.[133]

2.3.2.4. Polymerization Control by Viscosity

The determination of viscosity can be very useful also for the synthesis of polymers because the flow behavior is responsive to properties such as molecular weight and molecular weight distribution, hence, it can be helpful when following the course of a reaction. Such measurements can be employed as a quality check during production or to monitor and/or control a process. They are also a way to predict and control a host of product properties end use performance and material behavior.[134-137]

A variety of instruments is available to determine viscosity. They vary in cost, time required for measurements, operator skill required, sturdiness, precision, accuracy, and ability to measure shear rate variability or time dependency effects.[138] What they all have in common is the need to control temperature, as the viscosity strongly depends on it, so the measurement must be carried out under a constant and known temperature.[139-141]

Essentially there are two types of instruments, rheometers and viscometers. Rheometers are mostly used for deeply study viscoelastic behavior of non-Newtonian liquids; it measures the rheology of the fluid. Viscometer are used for Newtonian fluids, where viscosity does not vary with flow conditions.

Among viscometers there are the capillary viscometer in which the time required for a known amount of liquid to flow through a capillary tube is measured while viscosities can be calculated based on the diameter of the capillary. It is appropriate for determining the viscosity of volatile liquids or solutions containing volatile solvents, since they are essentially closed systems. Another instrument is the bubble viscometer that is widely used in quality control to approximate the viscosity of solutions of resins. The measurement is based on the rate of rise of an air bubble in a tube filled with a liquid. The higher the viscosity, the slower the bubble rises. They are only appropriate for Newtonian transparent fluids. The most widely used control device for measuring flow of industrial coatings, especially for spray application, is the efflux cup. The functioning is simple, one holds a thumb over the hole in the bottom of the cup, fills the cup with coating, removes the thumb, and then determines the time at which there is a break in the stream of coating flowing through the hole, the result is expressed in seconds. Another massive used instrument is the rotating disk viscometer. The liquid is contained in a thermostated container (stator) where a disk (rotor) is immersed in it and rotated by a motor over a range of rpm. The torque required to rotate the disk at a certain rpm is measured, and viscosity is given in mPa·s. The viscosity C_V (in poise) for Newtonian fluids is then given by:

$$C_V = 2.5G(\frac{1/R_1^2 - 1/R_2^2}{\pi h\omega}) \quad (28)$$

where *G* is the couple (Nm) formed by the force exerted by the torsion wire and its deflection, R_1 and R_2 are the radii of the inner and outer cylinders, *h* is the length of the cylinder, and ω is the angular velocity of the rotating cylinder.

Rotational viscometer (Figure 24) is widely used for the analysis of solvent-based wire enamels.

Figure 24. A rotating disk viscometer. Note: from http://www.thermo.com.cn/.

2.3.2.5. Polymerization Control by GPC Monitoring

Chemical information about polymerization process can be gained from gel permeation chromatography (GPC), known alternatively by its more descriptive name, size exclusion chromatography (SEC). GPC is a liquid chromatography that differs from other liquid chromatography techniques for its mechanism of retention, which depends on the size of the eluted species and not on chemical or physical interaction between the species and the stationary phase. In fact, chromatographic columns are packed with small (about 10 μm) silica or polymer particles (cross-linked polystyrene-divinylbenzene) containing a network of uniform pores into which solute and solvent molecules can be eluted. Molecules much larger than the average pore size of the packing are excluded from the pores, travel short distances, and they take less time to get to the detector, hence display low retention times. Instead, molecules having diameters much smaller than the pores can penetrate or permeate throughout the pore maze, travel long distances, and thus display high retention times. Between these two extremes there are intermediate-size molecules whose average penetration into the pores of the packing strictly depends on their diameters.

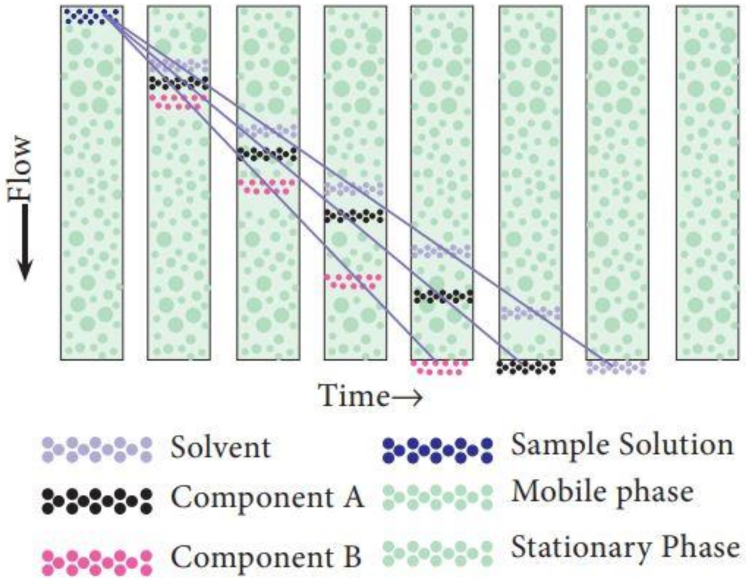


Figure 25. Size exclusion in the GPC column. Component B is the biggest species in the solution, component A is smaller than component B but bigger than solvent. Note: from https://cdn.technologynetworks.com/.

The detector usually is a differential refractive index (RI detector) which measures the refractive index of an analyte relative to the solvent. Differential refractometers contain a flow cell with two parts: one for the sample and one for the reference solvent. The detector measures the refractive index of both components. When only solvent passes through the sample component, the measured refractive index of both components is the same, but when an analyte passes through the flow cell the two measured refractive indices are different. The difference appears as a peak in the chromatogram. RI detectors are temperature sensitive, and a good temperature control is essential if high sensitivity is required. Another detector is the differential viscosity detector. It measures the solution viscosity of materials as they elute from the column. Combining this with concentration information from the other detector provides significant insight about the behavior of polymer molecules in solution.[142-143]

A typical calibration curve obtained analyzing samples of known molar masses, shows a lower limit of retention times (total exclusion) and an upper limit of retention times (total permeation) beyond which species with different sizes are not separated at all. Instead, in the selective permeation region, species are adequately resolved depending on their size.[144-145]

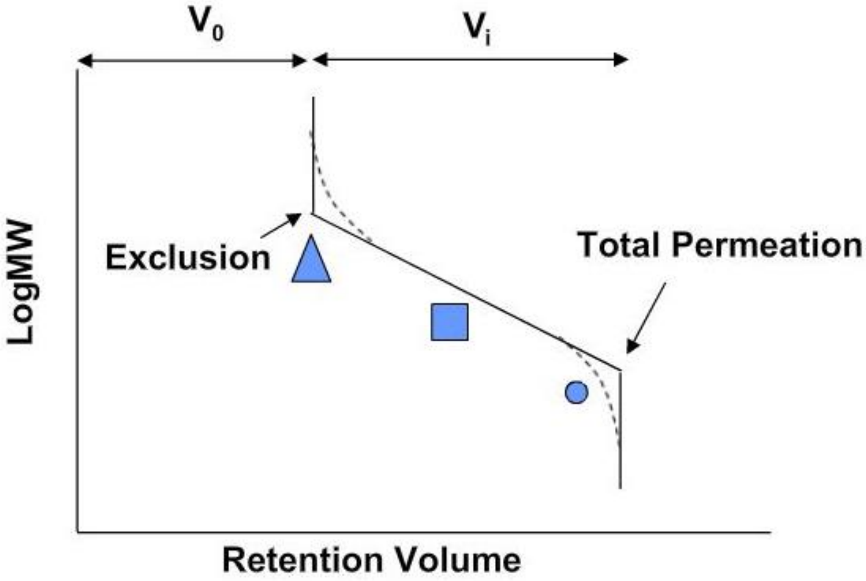


Figure 26. Permeation region of a GPC chromatogram. Note: from https://www.materials-talks.com/.

Actually, the term “size”, does not describe well the parameter which govern the retention time of a species; this is because the eluted molecules need to be considered together with their environment and in a dynamic way. In fact, a better parameter to consider is the hydrodynamic volume, which is the time-averaged molecular volume of a species, in addition to the volume of the solvent molecules associated with it.[146] By a computational approach, a GPC analysis of a polymer with a certain molar mass distribution can reveal that distribution and its average molar masses. A typical mass distribution for a synthetic polymer sample is shown in Figure 27, with related averages.

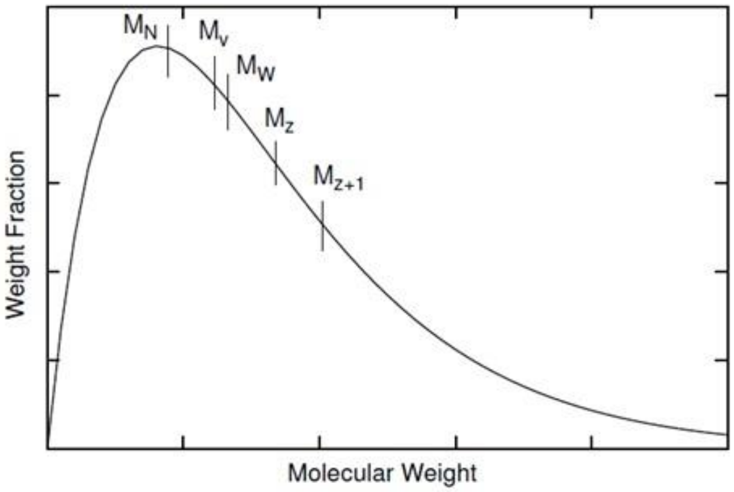


Figure 27. Typical molecular weight distribution of a polymer. Note: Adapted from Narin J. A. Oregon State University, 2003.

The number-average molar mass *Mn* is defined by:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \tag{29}$$

where N_i is the number of chains of species *i* of molar mass M_i. A weight-average molar mass M_w is instead defined as

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{30}$$

A higher average, the *z*-average molar mass, is given by

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} \tag{31}$$

which gives an even higher useful average, the ($z+1$) average molar mass, often required when describing mechanical properties.

$$M_{z+1} = \frac{\sum N_i M_i^4}{\sum N_i M_i^3} \tag{32}$$

Another important parameter to considered is the polydispersity index *PDI*:

$$PDI = \frac{M_w}{M_n} \tag{33}$$

PDI is used to indicate the distribution of polymer chain molecular weights in a given polymer. For a monodisperse polymer, or uniform polymer, *PDI* is close to 1, while values > 1.7 are common to a broad size (e.g., polydisperse) distribution of particles. For step-growth polymerizations, *PDI* is usually about 2.[125]

2.4. Environmental Impact

Polymeric materials offer many advantages for specific applications. They are easy to shape, do not corrode or decompose, but slowly, and the characteristics can be adapted to the specific needs by using composites or adding specific layers or additives. Contrary to popular belief, polymeric materials are extremely resource efficient along their service life, helping us to avoid food waste, to save energy and to decrease CO_2 emissions. For example, polymeric insulation saves 250 times the energy used for its production. Thanks to plastic parts, cars have four times lower environmental impact and plastic packaging extend significantly the shelve life of food reducing spoilage and waste. Moreover, food packaging reduces in many countries the risk of spreading diseases, making sterile food and water.[147-149]

On the other hand, the worldwide production of plastics we have today needs a large amount of energy and resources and, nevertheless, cause a large amount of waste and greenhouse gas (GHG). Today saving sources and reduce CO_2 emissions are two of the most important topics that need to be considered when dealing with producing any necessities.

These new challenges affect the whole lifecycle of polymeric materials, from production to processing and finally recycling, and new developments are needed to match them.

In the field of wire enamels, one way to reduce the environmental impact is the use of bio-based monomers and solvents and thus limit dependence on petrochemical sources.

2.4.1. Bio-based Economy

The bio-based economy overcomes these problems by using renewable resources and eco-efficient processes to produce sustainable bio-products and bioenergy. This model does not depend on fossil materials, but it is based on resources that can be replenished naturally over time such as biomass. This term refers to any organic matter available on a renewable basis and it is divided into primary and secondary biomass. The first comes directly from plants, animals, or aquatic algae; the second comes from wastes produced from primary biomasses (forestry residue, agriculture, industrial and municipal solid waste). The use of biomass waste not only allows a renewable approach for energy, but it is also a potential strategy for recycling municipal solid waste. Consequently, biomass is considered a renewable and abundant energy resource with zero emissions, and it can be used to replace fossil oil and gas, closing the carbon cycle.[150]

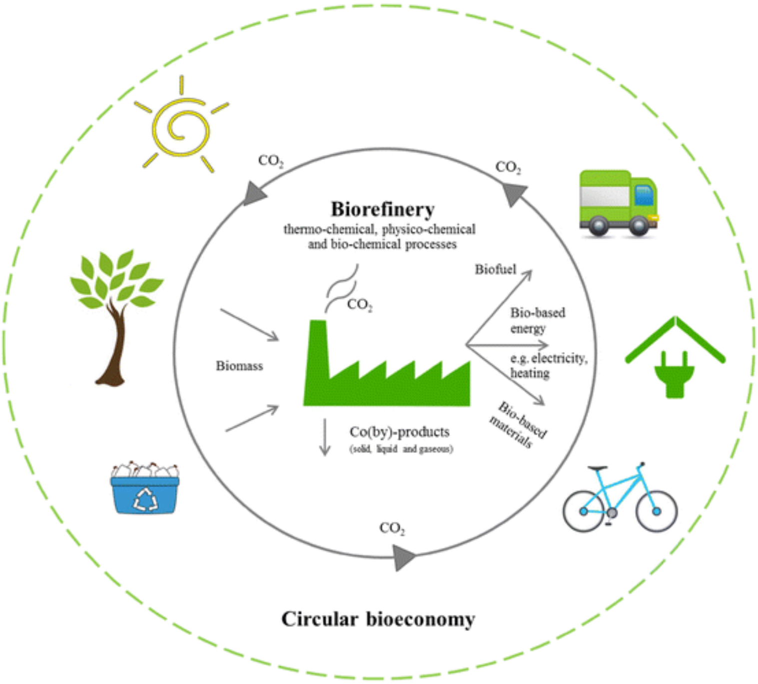


Figure 28. Biomass conversion for circular economy. Note: from Zuin, V. G. et al. Top Curr Chem (Z) 2018, 376 (1), 3.

Biomass is converted into high-value applications by bio-refineries, which represent the key component for the bioeconomy (Figure 28). It includes all the technologies capable of making sustainable use of biomass, transforming it into a wide range of chemicals, materials, fuel, feed, and energy.[151-153]

2.4.2. Bio-based polymers

Biopolymers offer a renewable alternative to traditional petroleum-based plastics and can be derived from a wide variety of feedstocks including agricultural products such as corn or soybeans and from alternative sources like algae or food waste.[154-156] Biopolymers can replace petroleum-based polymers in nearly every function from packaging and single use to durable products. However, being derived from renewable resources does not guarantee that biopolymers will perform favorably when compared to petroleum-based polymers, and as such, sustainability assessments like LCA are conducted to compare and improve the environmental impacts of biopolymers.[157]

The definition of biopolymer is influenced by the source of the raw materials and the biodegradability of the polymer. Generally, they are divided into three categories.[158]

1. Biopolymers that are biodegradable and are made from renewable raw materials.
2. Biopolymers that are not biodegradable and are made from renewable raw materials.
3. Biopolymers that are biodegradable and are made from fossil resources.

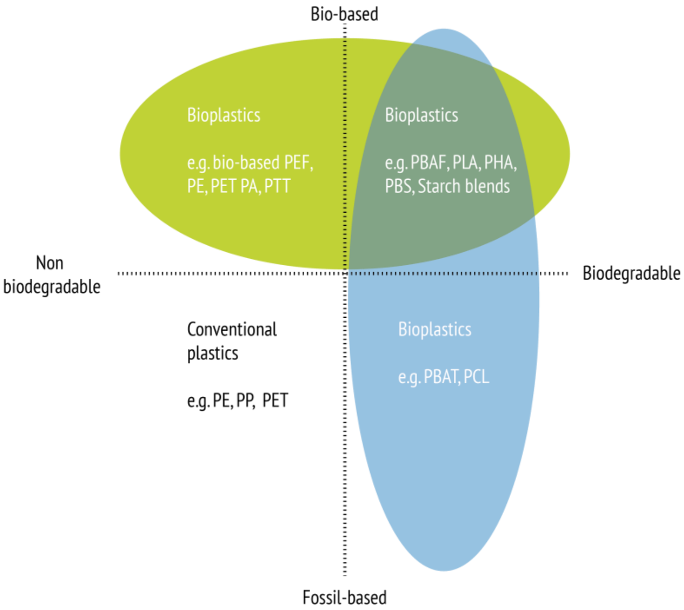


Figure 29. Classification of bioplastics. Note: from https://www.european-bioplastics.org/bioplastics/.

In the field of wire enamels, biodegradable polymer would not be ideal due to the high thermal and mechanical stress to which insulators are subjected, hence, possible biopolymers could be those belonging to the second category: polymers that are not biodegradable but are made from renewable raw materials like biomasses.

2.4.3. Bio-based solvents

Bio-based solvents are a highly sought-after class of bio-based products.[159] Typical examples are ethanol, glycerol, 2-methyltetrahydrofuran and limonene. A sustainable chemical industry will depend on the availability of renewable solvents, and much is being done at national and international regulatory and standardization levels to facilitate the introduction of bio-based products, including solvents. In the EU, for example, a strategy for implementing and encouraging a bioeconomy has been launched and a mandate has been issued specifically for the development of standards for bio-based solvents.[160-161]

As a tool to support and strengthen the bioeconomy, the aim of standards is to increase market transparency and establish common requirements for products in order to guarantee certain characteristics such as a minimum value of bio-based content.[162] Bio-based solvents also have to compete economically with established petrochemical solvents to gain significant market share. The first result of this standardization work, a technical specification for bio-based solvents, has now been published for the benefit of business-to-business (B2B) transactions.[163]

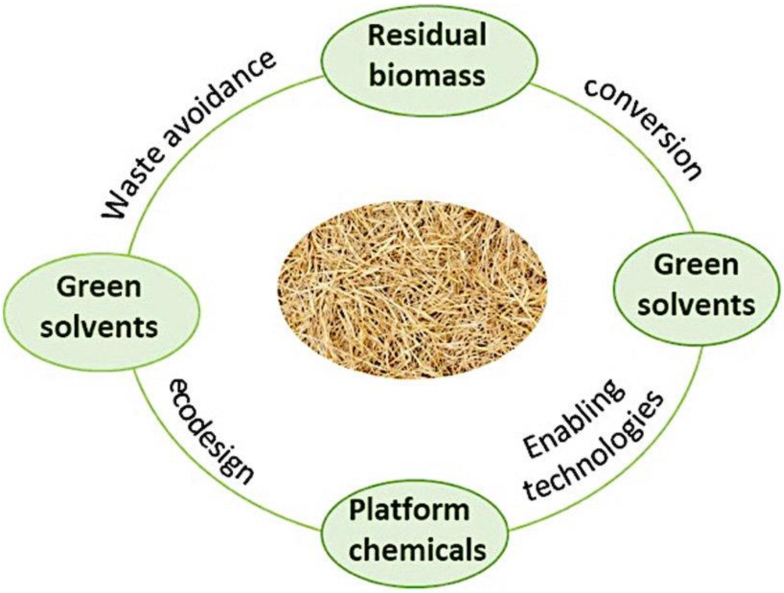


Figure 30. Circular economy with biomass derived green solvents. Note: from Grillo, G. et al. Molecules 2021, 26, 798.

The conversion of renewable resources and biomass into sustainable feedstocks are an important alternative to meet the increasing demand for energy and chemicals.[164] Biomass could provide the raw materials and reaction media necessary for modern industrial applications.[165-167] One important class of bio-renewable compounds are sugars and their polymer derivatives.[168] The conversion of sugars, for example cellulose, to oxygenated commodity chemicals is extensive.[169] Importantly, some of these protocols were translated from the bench to industrial scale. One of the key drivers for the selective conversion of biomass to novel chemicals is the increased regulatory constraints placed on toxic, petroleum-based solvents that are the mainstay of industrial synthesis. The development of safer solvents is one of the core tenets of the Twelve Principles of Green Chemistry.[170] One reason behind the inclusion of solvents in this key list is that between 75-80% of waste associated with the synthesis of pharmaceuticals comes from solvents.[171] In order to combat the cost of solvents, in terms of time, expense and to the environment, a variety of solvent selection guides have been put forward.[172] One key class of solvent that currently does not have a direct replacement are dipolar aprotic, such as *N*,*N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP). Both solvents were added to the REACH restricted substances list, which severely limits their ability to be used as industrial solvents.[173-174]

PART II

EXPERIMENTAL SECTION

In this section, three different studies are reported. The first study is aimed at replacing the common used solvent *N*-methylpyrrolidone (NMP) with less harmful ones for the synthesis of NMP-free polyamide-imides and polyamic-acids (polyimides after curing). This work is addressed to chapter 4.

Solvent Replacement

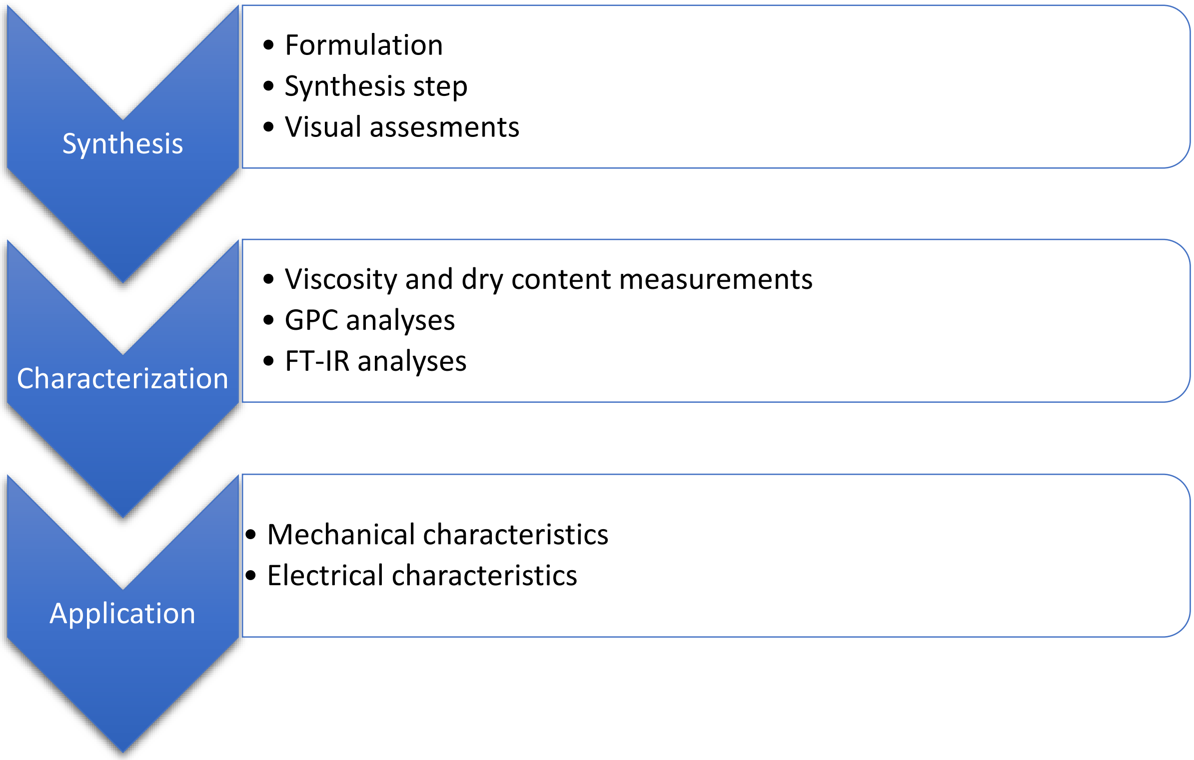
Polyamide-imide (PAI)	• Cyrene • *N*-formylmorpholine (NFM)
Polyimide (PI)	• Cyrene • 3-methoxy-*N,N*-dimethylpropionamide (MDMP)

The second part is focused on replacing harmful and petroleum-based diamines with bio-based ones for the synthesis of polyamic-acids (polyimides after curing) and polyester-imides. This work is addressed to chapter 5.

Monomer Replacement

Polyimide (PI)	• Bio-based diamine 1 (BD1) • Bio-based diamine 2 (BD2) • Bio-based diamine 3 (BD3)
Polyester-imide (PEI)	• Bio-based diamine 1 (BD1) • Bio-based diamine 2 (BD2) • Bio-based diamine 3 (BD3)

Whenever possible, molecular weight distributions of the batches were studied by GPC. In order to evaluate the effective characteristics of the synthetized wire enamels, all the batches, when possible, were applied and cured on copper wires by company’s operators, following an internal standardized enameling procedure. Then, enameled copper wires were tested following procedures described in chapter 1.4.



Many attempts have led to resins which do not meet the minimal requirements to be used as wire enamels. However, those resins could be used in the specialty coating industry. In this sector coatings are applied to parts like cookware, for example cooking pans, to prevent corrosion. These applications have not been thoroughly investigated because the tools to carry out these specific tests are not available as the main sector of the company is electrical insulation. Finally, in chapter 6, quantitative determination of isocyanate monomer in PA resins is described.

3. Materials and Methods

3.1. Materials

All reagents and solvents were purchased from commercial suppliers and used without further purification, unless mentioned otherwise. The quality of different compounds is guaranteed from the internal CQ laboratory.

All the syntheses were carried out in a 2 liters round bottom glass vessel with a five-necked glass head and a mechanical stirrer. A mantle was used for heating. A laboratory vacuum pump and a distillation apparatus were used when mentioned.

3.2. Instruments and Methods

3.2.1. Gel Permeation Chromatography

GPCs were performed on a *Thermo Knauer* assembled instrument with a Smartline 1000 pump and a Smartline 2300 differential refractometric detector. The column system is composed of 3 columns in series: Agilent™ PLgel 10^4Å, 7.5 x 300 mm, 5, 10 and 15 µm respectively.
For PAI and PAA analyses, the eluent consisted in a solution of THF:DMF 50:50 with a buffer solution of H_3PO_4 and LiBr at 5.88 and 2.60 mg/ml respectively. For PEI analyses, the eluent was composed of a solution of THF:DMF 50:50. In both cases, the eluent and the column compartment was kept at 33°C.
Before analysis, resins were dissolved in the proper eluent solution at a solid content concentration of 50 mg/mL. Samples were then filtered with a 0.45 µm PTFE wheel syringe filter from Agilent™. 100 µL of each filtered sample was injected in the loop.

3.2.2. Infrared Spectroscopy

The instrument used was *Thermo Scientific Nicolet iZ10* with the *Smart Omni-transmission* accessory with a KBr support and with a diamond crystal ATR module. The recorded wavenumber range was from 450 to 4000 cm^{-1}. Spectra were recorded with an accumulation of 16 repeated scans for both the background and sample analyzes. The commercial software *Thermo Scientific™ OMNIC™ Series FT-IR* was used to process and calculate the wavenumbers associated to the absorption bands of their spectra.
Characterizations of liquid resins were performed by simply applying a thin layer of the product on a KBr plate (previously realized by finely grinded anhydrous KBr with the aim of a press), then the plate was stored in a laboratory oven for fifty minutes at 100°C to let the solvents evaporate; after this thermal treatment the analysis was performed. Characterizations of solid samples (as cured wire enamels) were performed using the ATR technique.

3.2.3. Viscosity Determination

Viscosity measurements were performed with a *Haake* viscometer at constant shear rate and at 23°C. All samples were measured without any dilutions. Viscosity values were reported in cPs (centipoises).

3.2.4. Solid Content Determination

Solid contents of resins were performed in the following way: 1 gram of sample was put on a metal disk and heated to 180°C for 1 h in an oven. The value was obtained with the following equation.

$$R.S.\% = \frac{W_2}{W_1} * 100 \tag{34}$$

Were W_1 is the weight of the sample before heating and W_2 is the weight of the sample after heating.

For Cyrene and NFM based polymers, 2 grams of sample were put at 200°C for 2 h due to their higher boiling point.

3.2.5. Amine Content

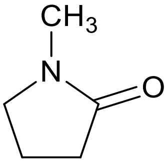
The amines were dissolved in glacial acetic acid and titrated with perchloric acid 0.1 N, in presence of crystal violet as indicator, until toning from purple to green was observed.

3.2.6. Software

Hansen solubility parameters were calculated using *HSPiP* software.

4. NMP-free Wire Enamels

One of the most common solvents for wire enamels is *N*-methylpyrrolidone or *N*-methyl-2-pyrrolidone (NMP) (Scheme 21). It is a polar aprotic solvent with a boiling point of 204.3°C at 101.3 kPa. NMP shows a low volatility, high thermal stability, high polarity, high hygroscopicity and noncorrosive properties vs metals. Thanks to these properties, NMP is an important solvent and reaction medium for the chemical industry.



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Scheme 21. N-Methylpyrrolidone.

NMP is produced industrially by treating butyrolactone with methylamine, via a typical ester-to-amide conversion.[175] Alternative routes include the partial hydrogenation of *N*-methyl succinimide and the reaction of acrylonitrile with methylamine followed by hydrolysis. About 20,000 to 30,000 tons are produced annually.[176] It is used as a solvent for surface treatment of textiles, resins, and metal coated plastics or as a paint stripper. It is also used as a solvent in the commercial preparation of polyphenylene sulfide. In the pharmaceutical industry, NMP is used in the formulation for drugs by both oral and transdermal delivery routes. It is also used heavily in lithium-ion battery fabrication, as a solvent for electrode preparation.

In the wire enamel industry, NMP is used as solvent and reaction medium for the synthesis of solvent-based polyamides, polyamide-imides and polyamic-acids. However, with increasing regulation of certain materials and compounds, NMP has recently come under scrutiny due to toxicological concerns. In particular, it has recently been reclassified as toxic to reproduction (H360) and was added in the SVHC list (Substance of Very High Concern) by the European Chemicals Agency (ECHA).[177-178] These drawbacks have created an interest in greener and safer solvents. The main difficult to find alternatives to NMP lies in the fact that very few solvents are able to solubilize highly polar polymer, especially if their molecular weight is high. In addition to solubility, the solvent must not react with the monomers during polymerization.

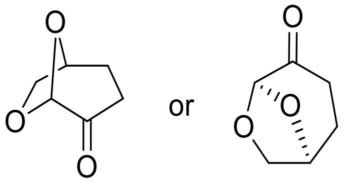
In the present work, three alternatives to NMP were examined based on company availability:

- Dihydrolevoglucosenone (Cyrene™)
- *N*-formyl morpholine (NFM)
- 3-methoxy-*N,N'*-dimethylpropionamide (MDPA)

These substances are not in the SVHC list, do not show reprotoxicity and have similar solvency properties to NMP.

- **Dihydrolevoglucosenone (Cyrene™)**

As said in chapter 2.4.3, biomass can supply a non-fossil feedstock for the production of bio-based solvents and, not less important, can provide a non-reprotoxic substance which is not under the SVHC list. An interesting polar and aprotic substance that is described in literature as capable of replacing NMP is the bio-available solvent Cyrene™ (dihydrolevoglucosenone or (1S,5R)-6,8-dioxabicyclo[3.2.1]octan-4-one)(Scheme 22).[179-180]



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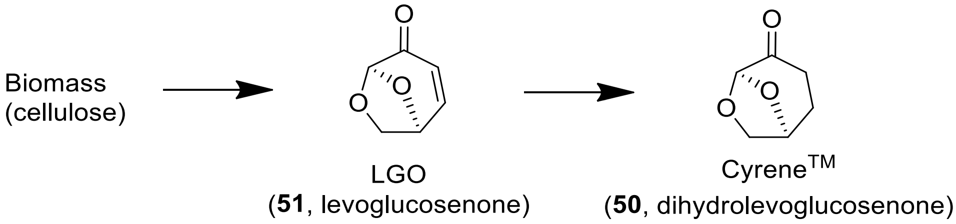
Scheme 22. Cyrene™.

Cyrene is a clear colorless, to light-yellow liquid with a mild, smoky ketone-like odor. It is miscible with water and many organic solvents. Its boiling point is 226 °C at 101.325 kPa. Cyrene is manufactured by Circa Group in a two-step process from waste cellulose on a 50 ton/year scale (
Scheme 23).[181-183]



Scheme 23. Methods for the preparation of LGO (1) and Cyrene (2).

Importantly, it has been shown that Cyrene is only barely ecotoxic (OECD No. 201, 202 and 209), has no mutagenicity (OECD No. 471 and 487) with a LD50 > 2000 mg/kg (OECD No. 423, acute toxicity method) and, unlike NMP or DMF has no reprotoxicity.[184]

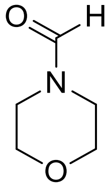
Cyrene has become interesting due to its chemical-physical properties, which are claimed to be similar to those of NMP, as presented by solvent producer in different occasions.[185-186]

In view of these convincing aspects, it was decided to synthetize polyamide-imide and polyimide precursor using Cyrene as solvent medium instead of NMP.

- ***N*-formylmorpholine (NFM)**

N-Formylmorpholine or morpholine-4-carbaldehyde (Scheme 24) is a colorless liquid with a faint amine-like odor. It is produced from morpholine and formic acid in a two-step process.[187]

N-Formylmorpholine is used by petroleum refiners as a solvent for the extraction of aromatics and also as an anticorrosive agent in fuel oil.



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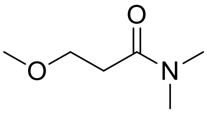
Scheme 24. N-formylmorpholine.

Its boiling point is 244°C at 101.3 kPa and has a good thermal stability. Its solvency properties are comparable to those of NMP and for this reason it has been used for the synthesis of polyamide imides.

- **3-Methoxy-*N,N*-dimethylpropionamide (MDPA)**

3-Methoxy-*N*,*N*-dimethylpropionamide or 3-methoxy-*N*,*N*-dimethylpropanamide (Scheme 25) is a colorless liquid with a faint amine-like odor. Like NMP, this solvent is polar and aprotic, hygroscopic and shows low volatility but is not classified as reprotoxic. The boiling point is 205°C at 101.3 kPa.



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Scheme 25. 3-Methoxy-N,N-dimethylpropionamide.

MDPA is often used instead of NMP in the electronic industry due to health limitations of the latter.[188] This solvent has been already investigated and reported in the literature for its use in polyamide-imides and it will be taken into consideration only for the synthesis of polyamic-acids.

These 3 solvents have been studied using Hansen solubility parameters (see chapter 2.2.1.1). Dihydrolevoglucosenone, NFM and MDPA have been mapped in the Hansen space and compared to most common dipolar aprotic solvents (Table 5).

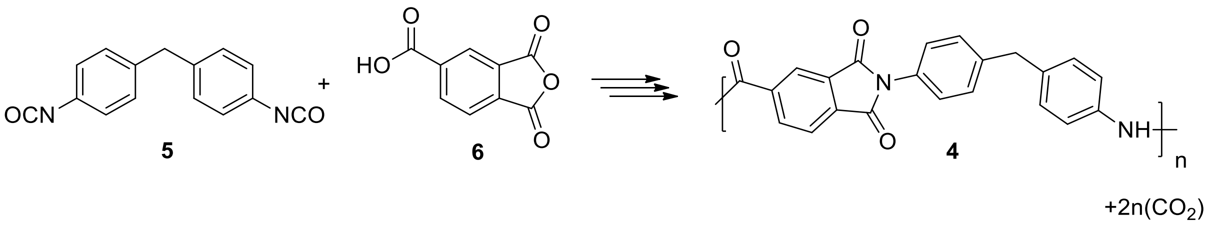
Table 5. Hansen solubility parameters of some dipolar aprotic solvents.

	Cyrene	*NFM*	*MDPA*	*NMP*	*DMF*	*DMAc*	*DMSO*
δ_d [a]	18.9	16.6	17.1	18.0	17.4	16.8	18.4
δ_p [a]	12.4	11.7	10.5	12.3	13.7	11.5	16.4
δ_h [a]	7.1	10.0	8.9	7.2	11.3	10.2	10.2
b.p. (°C)	226	244	205	204	153	165	189

[a] *calculated with HSPiP software.*

4.1. NMP-free PAI Wire Enamels

Polyamide-imides were synthetized according to the generic diisocyanate route (chapter 2.1.1.2). Molar ratio between TMA and MDI was always kept to 1 to 1.01 respectively. This excess of MDI is added because diisocyanates, being very reactive, contain dimers and trimers that lower the final -NCO content. This excess will balance the stoichiometry of the reaction, bringing it towards a ratio of about 1:1. For a more detailed mechanism, see chapter 2.1.2.2.b.



Scheme 26. Generic synthesis of PAIs.

Synthesis of PAIs is described herein. In a 2 L five-necked round bottom glass vessel, equipped with a mechanical stirrer and a thermocouple, solvent (NMP, Cyrene or NFM) and trimellitic dianhydride is added at room temperature and the stirrer is turned on. Temperature is set to 50°C in order to solubilize the monomer. After solubilization, MDI is added slowly to avoid a steep rise in temperature and excessive foam formation due to the strong exothermicity of the reaction. Thereafter, the reaction temperature is increased stepwise from 50°C up to a maximum of 150°C until the viscosity reaches 50,000 – 60,000 cPs. As the viscosity of polymers changes depending on the solvent used, there is not a unique target viscosity that must be achieved when making PAIs in solvent other than NMP. For this reason, an arbitrary range of 5,000 – 10,000 cps was chosen as the final viscosity to be reached before stopping the reaction for the PAIs made in Cyrene, NFM and MDPA. When the designed viscosity is reached, the reaction is cooled down to 80°C and benzylic alcohol and thinners (xylene, naphthas or a mixture of them) are added to quench the reaction and lower the viscosity in order to be cured on copper wires by the enameling oven. Filtered resins were then cured and enameled in the horizontal oven "MAG HEL4/5" owned by Elantas. Resulting magnet wires were subjected to mechanical, electrical and thermic tests (see chapter 1.4). Liquid resins were characterized by GPC and IR spectroscopy.

First, a generic synthesis of a PAI in NMP is performed in order to compare characteristics of liquid and cured resin to those of PAIs made in alternative solvents.

4.1.1. Synthesis and Characterization of Standard PAI in NMP

The synthesis of a PAI in NMP followed the procedure described in the previous paragraph. This batch, named IL11, is considered as PAI reference. During the synthesis, samples of resin were collected every hour to perform viscosity measurements (Table 6, Figure 31).

Table 6. Viscosity values measured at 20°C during the reaction.

Sample	*η (cPs)*
C1	200
C2	500
C3	2220
C4	5300
C5	10120
C6	12840
C7	15080
C8	15510
C9	16450
C11	17740
C12	19230
C13	19450
C14	23020
C15	25970
C16	27620
C17	30100
C18	35910
C19	48410

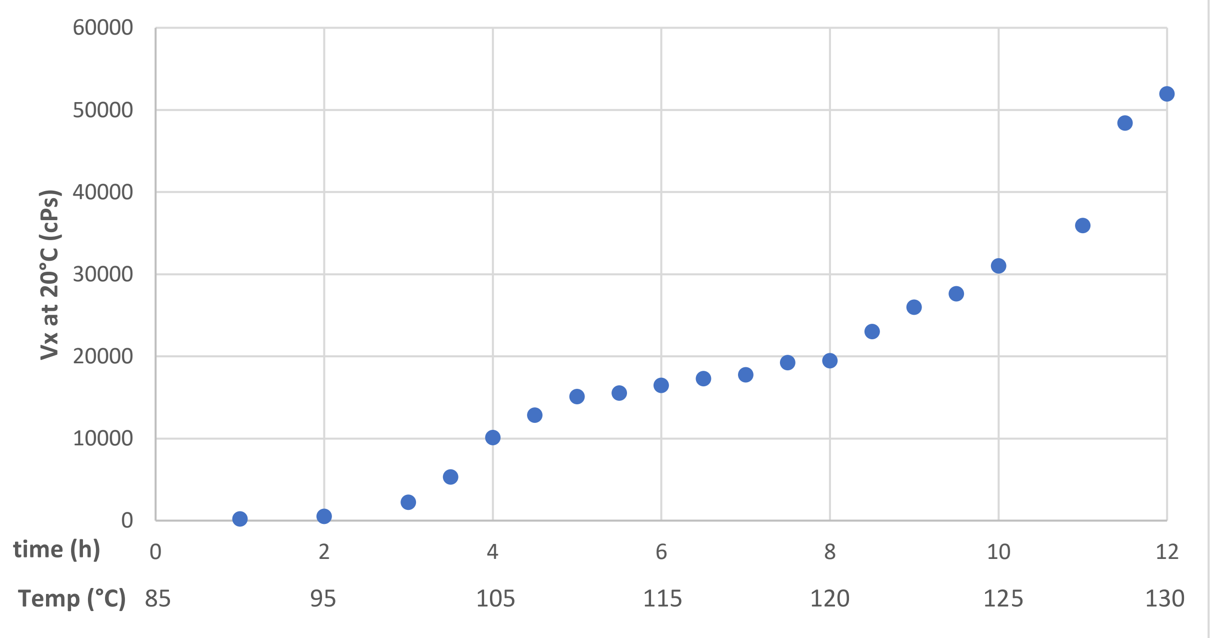


Figure 31. Viscosity values in function of reaction time and temperature.

The first sample was collected after 1 hour since the temperature had reached 85°C. As it can be seen, the curve rises in the first 5 hours, until the temperature reaches 105°C. This is the first stage of reaction, where most of the MDI reacts with TMA forming oligomers. After the plateau, when the temperature has been increased to 120°C, the viscosity raised again until the target value. At this point the polymerization has to be stopped as to not increase the viscosity too much. IR spectroscopy and GPC characterizations were performed on each sample collected (Figure 32, Figure 34). A drop of liquid enamel was spread on a metal sheet and heated to 240°C for 15' to evaluate the aspect of the cured film. After the dilution and filtration, the batch was applied and cured on copper wires and the resulting enameled wire was subjected to mechanical, electrical and thermal tests (see chapter 1.4 for a detailed description of the tests). Solid content was calculated as described in chapter 3.2.4.

Table 7. Synthesis parameters and characteristics of the liquid resin.

Batch	*Solvent*	*Monomers [wt%]*	*Temperature* [a] *[°C]*	*η [cPs]*	*S.C. [%]*	*Appearance*
IL11	NMP	37	130	51900	36.5	clear

[a] *Maximum temperature reached during the synthesis.*

Molecular weight parameters were calculated via software, after a proper calibration, on the last sample collected (C20).

Table 8. Molecular weight parameters.

Batch	*Mw*	*Mn*	*Mw/Mn*
IL11	24865	18374	1.35

Characteristics of the cured resin and results of tests conducted on the enameled copper wire are reported herein.

Table 9. Characteristics of the cured enamel.

Batch	*Film aspect*	*Wire aspect*	*Jerk test*	*Flexibility [%]*	*Cut-through [°C]*	*Tgδ [°C]*
IL11	good	good	passed	25	400	275

GPC were conducted on each liquid sample collected during the polymerization. Five of the twenty analyzed samples (C4, C5, C13, C17 and C20) are shown. Their chromatograms are depicted below.

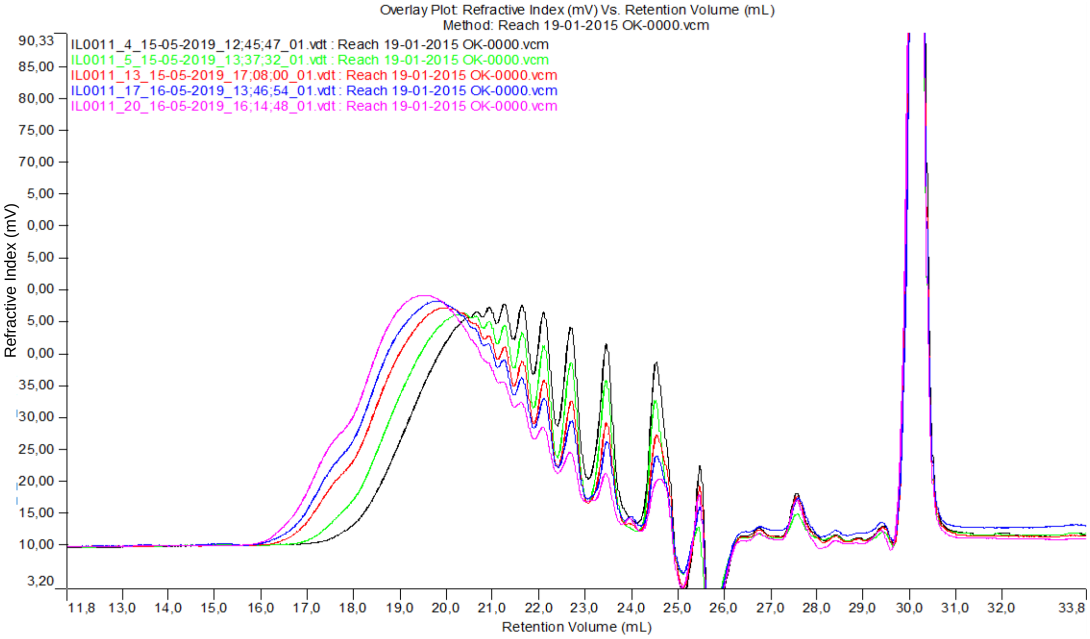


Figure 32. GPC chromatograms of IL011.

The GPC chromatograms obtained confirm the progress of the synthesis until the desired grade of polymerization. It can be noted that there is almost the same difference between the C4-C5 and C5-C13 samples, although the reaction time was very different (samples were taken every hour). This behavior reflects the trend of the viscosity values which remain almost constant from C6 to C10.

In order to evaluate the presence of other evident variations in the FT-IR spectrum of the PAI during the synthesis, the spectra between C1 and C20 were compared. Three of these spectra were provided in Figure 33 and Figure 34 (C3, C11, C20).

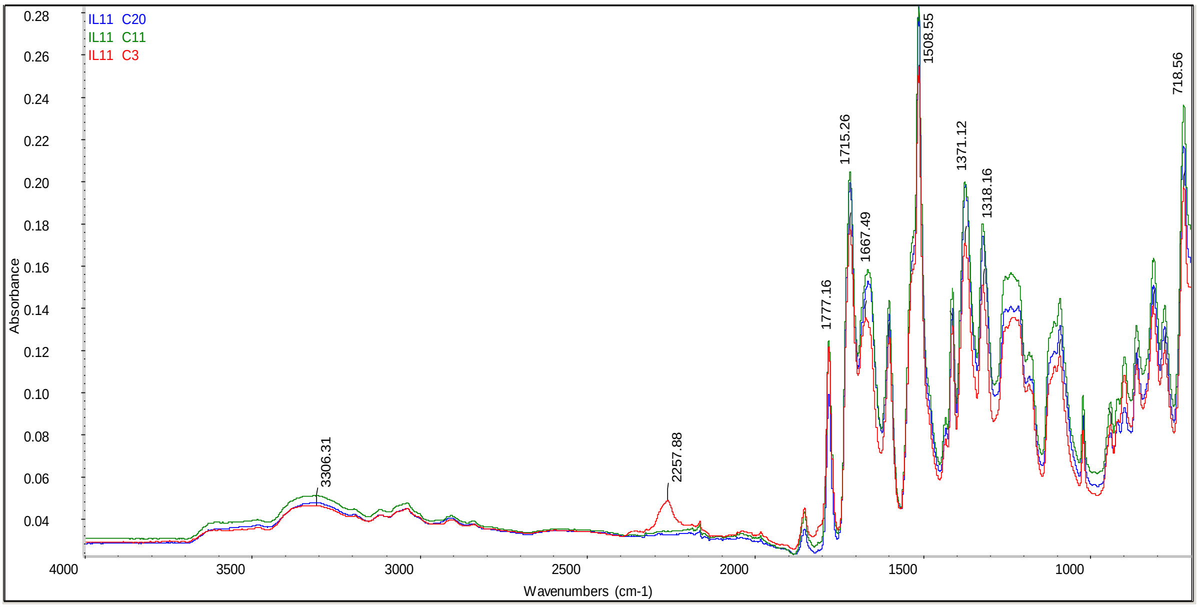


Figure 33. PAI spectra of samples C3, C11, C20 of batch IL11.

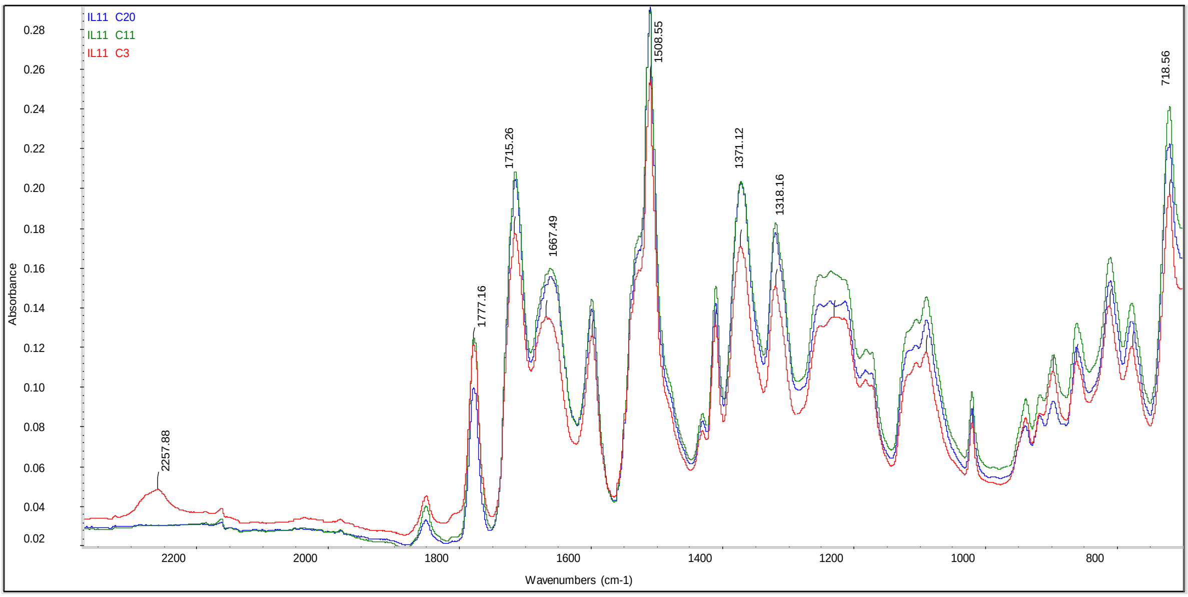


Figure 34. PAI spectra (samples C3, C11 and C20) focused on wavenumber between 700 to 2400 cm^{-1}.

IR spectroscopy shows characteristic bands of a polyamide-imide:[189]

- Imide: symmetric and asymmetric stretching of C=O, respectively at 1715 and 1777 cm^{-1};
- Imide ring: stretching at 1371 and 720 cm^{-1}.
- Amide: stretching of C=O (amide I) located at 1665 cm^{-1}.

- Amide: bending of N-H (amide II) at 1510 cm^{-1}.
- Amide: stretching of N-H at 3401 cm^{-1}.

Apart from the disappearance of the NCO band at 2258 cm^{-1} and a slight decrease in the anhydride bands (symmetrical and asymmetrical stretching of C=O, respectively at 1850, 1774 cm^{-1}) there are no other important changes in the PAI spectra during polymerization.

4.1.2. Synthesis and Characterization of PAI in Cyrene

The synthesis of PAI in Cyrene followed the procedure described in chapter 4.1. Only three attempts were made due to low amount of solvent available. In the first and second attempts the solvent medium was used at different concentrations. The third attempt derived from example A3 of the patent owned by Huntsman which is the only existing patent claiming the synthesis of polyamide-imides in Cyrene.[190] The patent claims to use a mixture of 63% of Cyrene and 37% of cyclohexanone as reaction mediums for the synthesis of PAIs. Cyclohexanone was added in order to shift the δ_d of the solvent mixture near to that of NMP and shift its Hansen point closer to the sphere of the polymer (Table 10).

Table 10. Hansen solubility parameters of Cyrene, cyclohexanone and NMP.

	Cyrene™	*Cyclohexanone*	*NMP*
δ_d ^{a}	18.9	17.8	18.0
δ_p ^{a}	12.4	6.3	12.3
δ_h ^{a}	7.1	6.1	7.2

^{a} calculated with HSPiP software.

In the first attempt (EL16), at around 95°C, the reaction was cooled down due to a steep rise in viscosity and the resin gelled when it was cooled down to room temperature. EL23 was the only resin that was able to be applied on copper wire. Hence it was diluted and applied but it resulted to be brittle and fragile and the enamelled wire did not pass the jerk test. EL22 resulted in a mixture of unreacted monomers due to poor solubility with the solvent mixture.

Attempts and results are summarized in Table 11. Molecular weight distribution values are reported in Table 12. All batches were applied on metal sheets and cured at 240°C for 15’ to see their cured film aspect (Table 12). Solid content was calculated as described in chapter 3.2.4.

Table 11. Synthesis parameters and characteristics of the liquid resins.

Batch	*Solvent*	*Monomer content [wt%]*	*Temperature[a] [°C]*	*η [cPs]*	*S.C. [%]*	*Resin appearance*
EL16	CYR	37	95	gel	45.1	gel
EL23	CYR	19	145	4400	30.9	clear
EL22	CYR:CHO	19	145	369	32.0	hazy

[a] Maximum temperature reached during the synthesis.

EL16 and EL22 were not able to be analyzed by GPC due to their insolubility in the eluent system.

Table 12. Molecular weight distribution values obtained by GPC.

Batch	M_w	M_n	M_w/M_n
IL11	**24865**	**18374**	**1.35**
EL23	19541	6541	2.99

Characteristics of the cured resins and results of tests conducted on the enameled copper wire performed only with EL23, are reported herein. T_g measurements were performed because it was not possible to perform $Tg\delta$.

Table 13. Characteristics of cured resins.

Batch	*Film aspect*	*Wire aspect*	*Jerk test*	*Flexibility [%]*	*Cut-through [°C]*	*$Tg\delta$ [°C]*
IL11	good	good	passed	25	400	275
EL23	brittle	bad	failed	0	-	-

Gel permeation chromatography was performed on EL23, and it was superimposed with the reference PAI in NMP (IL011).

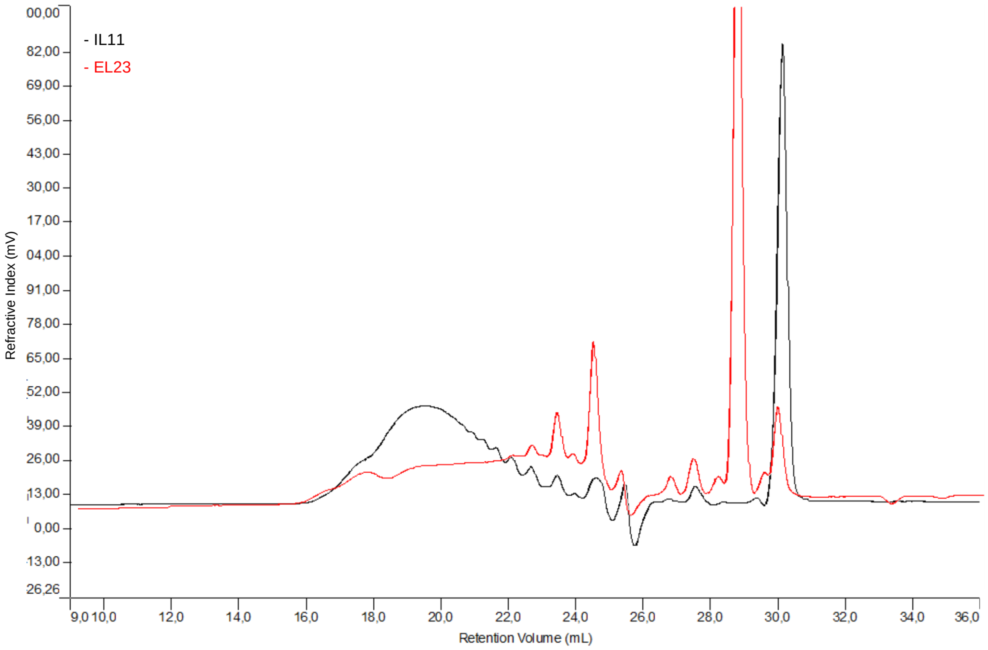


Figure 35. Overlapped GPC chromatograms between PAI in Cyrene (EL23, red) and PAI in NMP (IL11, black).

FT-IR spectra of EL23 is depicted below.

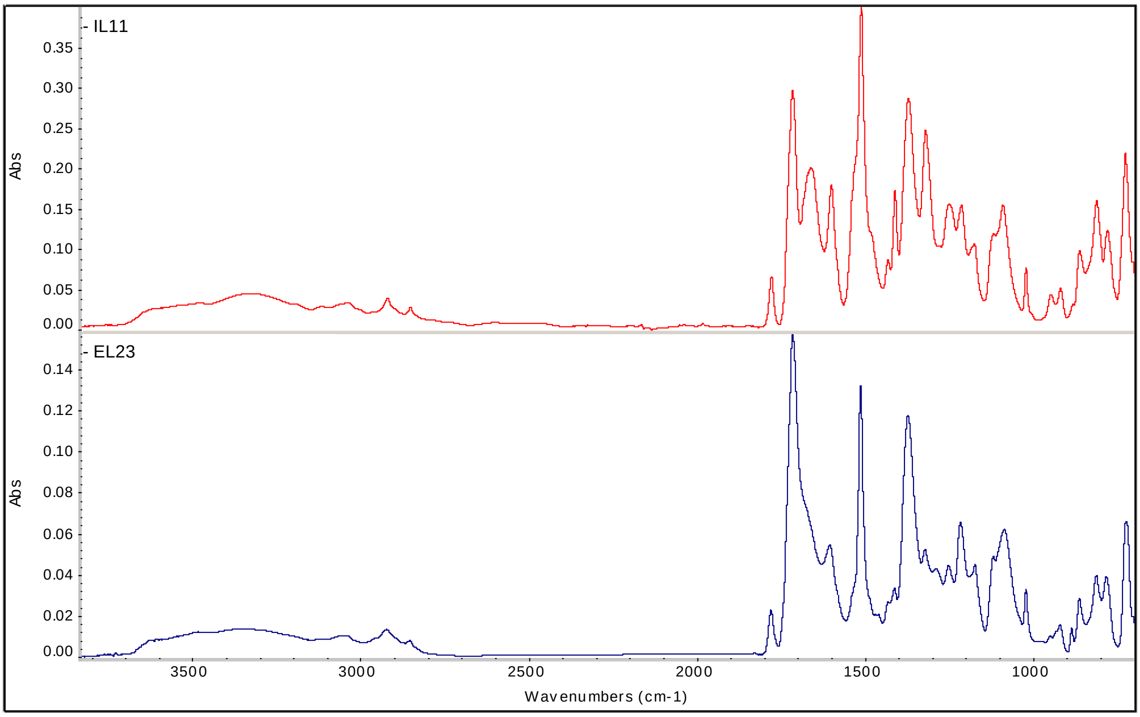
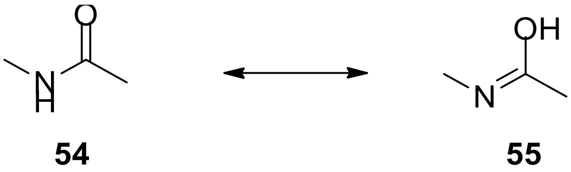


Figure 36. FT-IR ATR spectra of the standard PAI in NMP (top) and the NMP-free PAI enamel in Cyrene EL23 (bottom).

4.1.2.1. Discussion

From GPC, it is evident that the molecular weight distributions are not similar at all. EL23 is highly polydisperse and present also a high concentration of unreacted oligomers.
The most evident information from the FT-IR spectra is the absence of an evident band relative to the amide bond at 1650 cm^{-1} (amide I). First, it was supposed that the solvent might have reacted with the acid moiety of TMA since Cyrene is a cyclic acetal and acetals are not stable with acids. In order to investigate this hypothesis, Cyrene was mixed with TMA and stirred for 10h at 150°C in order to simulate the same reaction conditions. The resulting mixture EL24 was collected and ^{1}H-NMR was conducted (see chapter 4.1.2.2). ^{1}H-NMR spectra of EL24 only evidenced formation of trimellitic acid, derived from TMA, but no evidence of any reaction between the solvent and TMA is present. It was then supposed that the solvent might have modified the normal course of polymerization by blocking the amide formation. Cyrene could have stabilized the imidic form of the amide-imidic acid tautomerism (Scheme 27) (imidic acid band at 1600 – 1700 cm^{-1}) leading to cross-links between -NCO and -OH. An NMR study of EL16 was not possible due to its insoluble gel-like form.



Scheme 27. Amide-iminol tautomerism.

The gelling of the polymer when solid content gets higher, in EL16, is maybe explained by the incorporation of the solvent into the polymer chain caused by a strong hydrogen-bond interaction between the solvent and the polymer. In addition, hydroxy group of the imidic acid tautomer could have reacted towards isocyanates generating carbamate crosslinks (band at 1700 cm-^{1}). These two considerations can explain the increase of solid content from 37.46% to 45.10%.

The solvent properties of dihydrolevoglucosenone are very similar to NMP, however, laboratory tests have not been successful in the synthesis of PAIs. As seen before, different attempts to synthetize a PAI using Cyrene were carried out: both following an internal method and following the Huntsman patent resulted in a highly polydispersed polymer with poor mechanical characteristics and therefore impossible to be used in any application. In order to investigate side reactions involved, reactions between Reaction between Cyrene and TMA was set up separately and then characterized. IR and ^{1}H-NMR analyses, however, showed no evidence of reaction between Cyrene and TMA. It was then supposed that the solvent may have blocked the amide bond formation by stabilizing the imidic form of the amide-imidic acid tautomerism. Considering all the drawbacks, it was decided to close the project of Cyrene, considered a not suitable solvent for the production of polyamide imides.

4.1.2.2. NMR Characterization

- Compound **49**

^{1}H NMR: (500 MHz, $CDCl_3$) δ_H = 5.07 (s), 4.68 (s), 4.03 - 4.01 (d), 3.94 - 3.91 (m), 2.67 - 2.58 (m), 2.38 – 2.25 (m), 2,02 – 1.96 (m).

- Compound **6**

^{1}H NMR: (500 MHz, $CDCl_3$) δ_H = 11.98 (s, broad), 8.61 - 8.59 (d, double), 8.53 (m), 8.23 – 8.21 (d, double).

- Batch **EL24**

^{1}H NMR: (500 MHz, $CDCl_3$) δ_H = 13.65 (s, broad), 8.46 – 8.44 (d, double), 8.38 (m), 8.20 (m), 8.17 – 8.15 (d, double), 8.11 – 8.09 (d, double), 7.73 – 7.71 (d, double), 5.01 (s), 4.72 (s), 4.08 – 4.06 (d), 3.80 – 3.77 (m), 2.72 – 2.63 (m), 2.25 – 2.19 (m), 2.15 – 2.06 (m), 2.01 – 1.96 (m).

4.1.3. Synthesis and Characterization of PAI in NFM

After the results obtained from the solvent Cyrene™, *N*-formylmorpholine has been taken into consideration. Several attempts have been made and they have been summarized herein and in Table 15.

EL25 follows the standard procedure for PAI (see chapter 4.1). In EL27, the temperature of reaction was increased to obtain a higher molecular weight polymer. EL29 has a higher amount of monomers. In EL32 and EL37, a catalytic amount of water (0.03% wt) was added to try to increase the molecular weight of the polymer. Ethylene carbonate was added as co-solvent in EL33 and EL34, as a mixture of 80:20 (NFM:EtC) in order to shift Hansen parameters closer to those ones of NMP (Table 14). In EL33, EtC was mixed with NFM at the beginning of the reaction, while in EL34 it was added after the addition of MDI, trying to avoid side reactions with the latter. EL36, EL37 and EL38, have lower monomers content in order to avoid extremely high viscosities. In EL37 a catalytic amount of water was added.

Only EL25, EL27, EL33 and EL36 were applied and cured on copper wires in order to avoid problems to the enameling machine due to poor characteristics of the cured films of the other batches. It is important to clarify that no cross-link reaction takes place during the curing stage since no reactive sites are present on chain backbones of PAIs. PAIs are not cross-linked polymers.

Table 14. Hansen solubility parameters of NFM, ethylene carbonate and NMP.

	NFM	*EtC*	*NMP*
δ_d [a]	16.6	18.0	18.0
δ_p [a]	11.7	21.7	12.3
δ_h [a]	10.0	5.1	7.2

[a] *calculated with HSPiP software.*

Table 15. Attempts made with NFM.

Batch	*Solvent*	*Monomers content [wt%]*	*Temperature*^{a} *[°C]*	*η [cPs]*	*S.C. [%]*	*Resin appearance*
EL25	NFM	37.2	105	10500	37.2	clear
EL27	NFM	37.2	125	92000	38.1	clear
EL29	NFM	46.9	145	37960	42.7	hazy
EL30	NFM	37.2	135	31500	-	slightly hazy
EL32^b	NFM	37.2	115	240000	-	hazy
EL33	NFM:EtC	37.2	105	28000	38.5	hazy
EL34	NFM:EtC	37.2	95	3850	-	hazy
EL36	NFM	30.0	150	6000	30.37	clear
EL37^b	NFM	30.0	105	-	-	hazy
EL38	NFM	30.0	165	10000	32.2	slightly hazy

^{a} Maximum temperature reached during the synthesis. ^{b} Catalytic amount of H_2O was added.

In the following table, Mw, Mn and Mw/Mn values are depicted. EL37 was not able to be analyzed by GPC due to its insolubility in the eluent system.

Table 16. Molecular weight distribution values obtained by GPC.

Batch	*Mw*	*Mn*	*Mw/Mn*
IL11	**24865**	**18374**	**1.35**
EL25	10080	7190	1.40
EL27	11020	7743	1.42
EL29	16328	11259	1.45
EL30	11378	8060	1.41
EL32	14991	9368	1.60
EL33	21201	10661	1.99
EL34	104630	11347	9.22
EL36	11744	8190	1.43
EL38	14440	9389	1.54

Characteristics of cured resins and results of tests conducted on enameled copper wires are reported herein.

Table 17. Characteristics of cured resins.

Batch	*Film aspect*	*Wire aspect*	*Jerk test*	*Flexibility [%]*	*Cut-through [°C]*	*Tgδ [°C]*
IL11	good	good	passed	25	400	275
EL25	acceptable	rough	failed	0	295	255
EL27	good	rough	failed	0	235	225
EL33	brittle	rough	failed	0	221	203
EL36	acceptable	rough	failed	0	290	243

In the following figures, superimposed GPC chromatograms of EL25, EL27, EL30, EL36 are depicted (Figure 37).

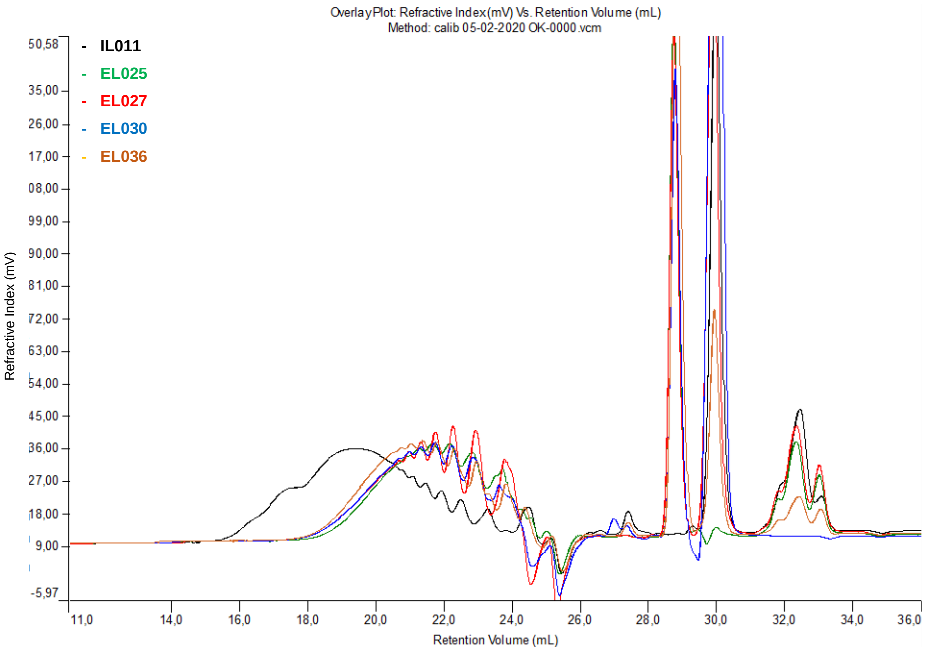


Figure 37. Overlapped GPC chromatograms of PAI in NFM (EL023, EL027, EL030, EL036) and PAI in NMP (black).

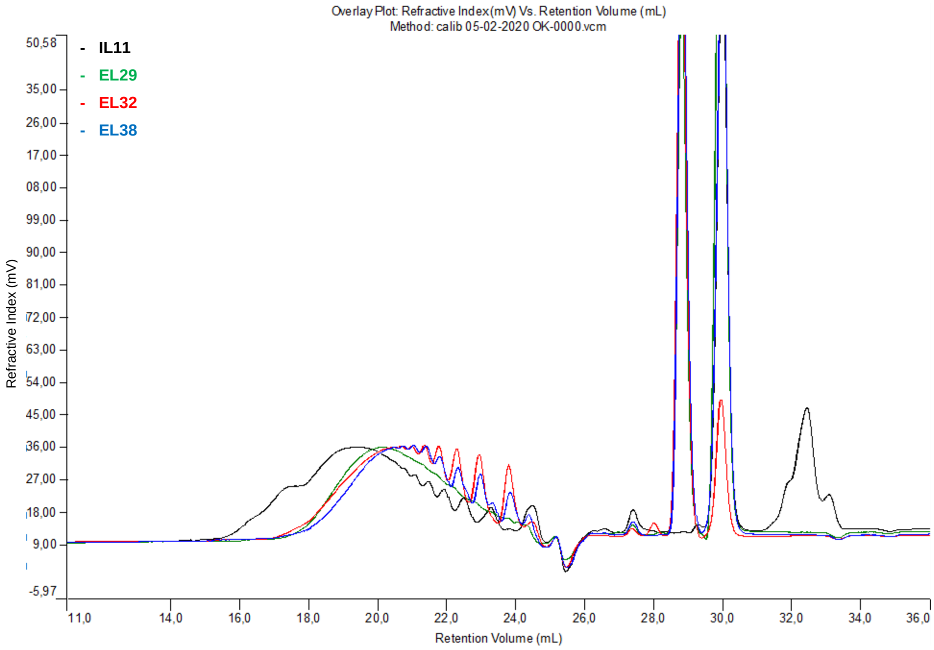


Figure 38.Overlapped GPC chromatograms of PAI in NFM (EL29, EL32, EL38) and PAI in NMP (IL11).

The following chromatogram (Figure 39) shows molecular weight distributions of EL33 and EL34 where ethylene carbonate was used as co-solvent.

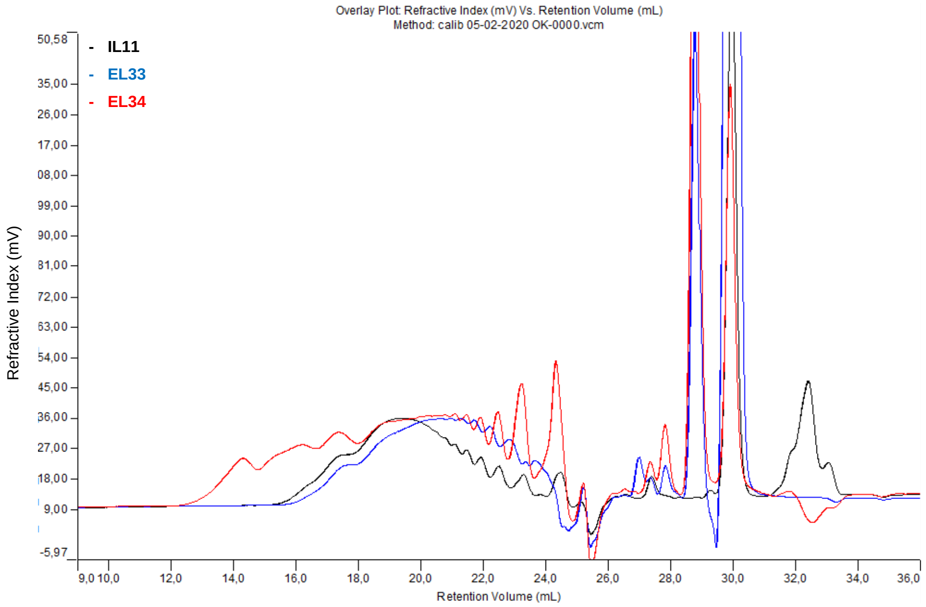


Figure 39. Overlapped GPC chromatograms of PAI in NFM and EtC (EL33, EL34) and PAI in NMP (IL11).

All the batches were analyzed by IR spectroscopy (Figure 40).

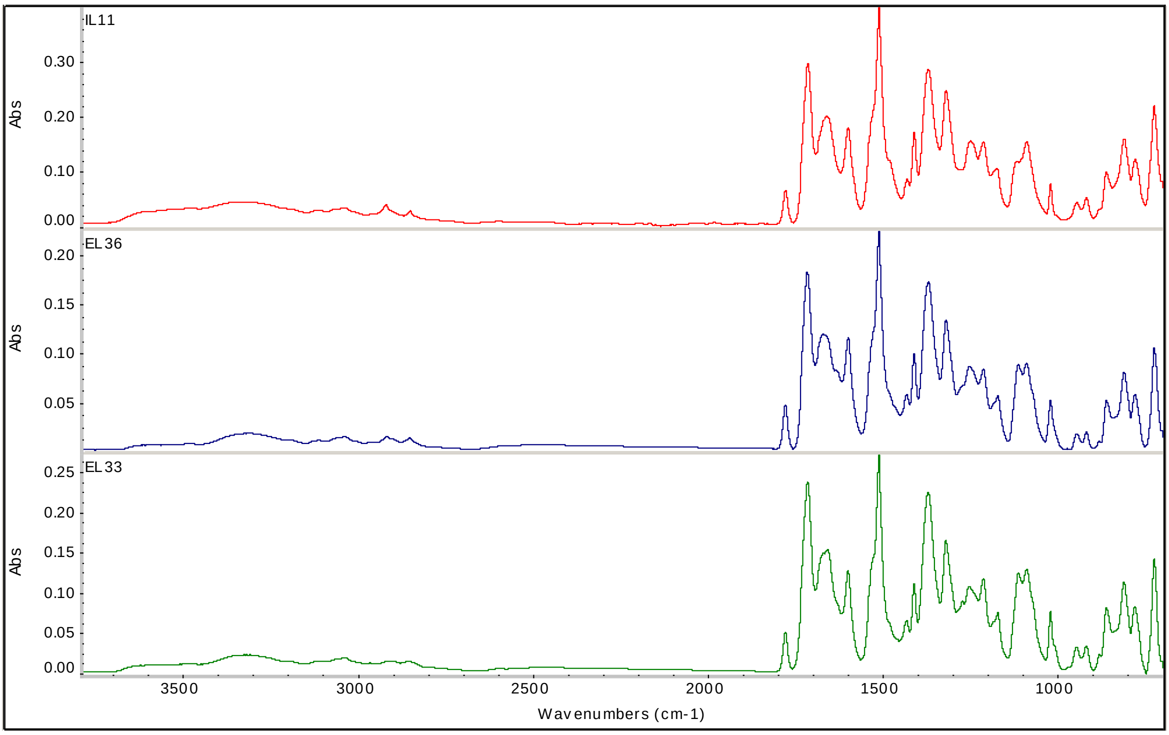


Figure 40. IR spectra of PAI in NFM (EL36).

4.1.3.1. Discussion

GPC of EL25, EL27, EL30, EL36 show low molecular weights and a high concentration of oligomers (Figure 37), a sign that the polymerization struggled to proceed.

Figure 39 shows molecular weight distribution of EL33 and EL34 where ethylene carbonate was used as co-solvent. In the first batch, ethylene carbonate was added after the addition of NMP. It seems to have a molecular weight distribution close to the reference. In EL34 ethylene carbonate is added after the addition of MDI. The molecular weight distribution is abnormally high and polydispersed due to the possible reaction between ethylene carbonate and MDI.[191]

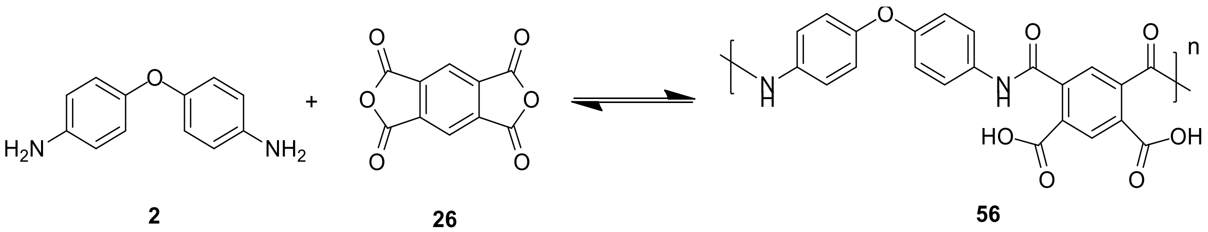
Looking at FT-IR spectra, in all of them, characteristic bands of polyamide imides are present. In addition, unlike GPC chromatography, all the batches seem to be similar to each other and to the standard PAI. Even the batches with ethylene carbonate do not show anomalies (Figure 40).

Looking at viscosities of the batches with the highest molecular weight (EL29, EL32, EL38 in Table 15), the viscosity values are way higher than the reference, but their molecular weight is still too low to have acceptable mechanical proprieties. This resulted in failing the jerk test. All the batches where ethylene carbonate was added as co-solvent (EL33, EL34), resulted in brittle films due to low evaporation rate of EtC during enameling phase.

The batch with the molecular weight distribution closest to the reference, excluding EtC, is EL32 (Figure 38), with a viscosity of 240,000 cps. It is obvious that in order to obtain an acceptable molecular weight, extremely high viscosities should be achieved, making the final product unsuitable as wire enamel, considering that it could not be handled to be applied on the wire, regardless the fact that the whole production process would be impracticable at such high viscosities. In addition, electrical characteristics are not acceptable to be used as wire enamels. The solvent *N*-Formylmorpholine proved to be unsuitable as reaction medium for polyamides-imides and in any case it was possible to obtain an enameled wire with acceptable properties.

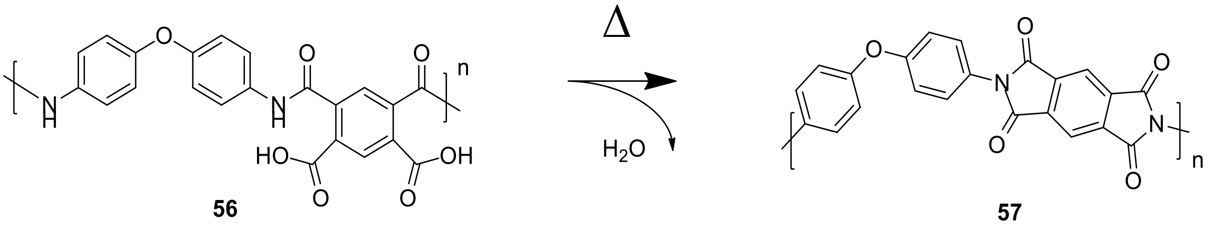
4.2. NMP-free PI Wire Enamels

Polyamide precursors, hence, polyamic-acids (PAAs), were synthetized following the standard approach which involves a polyaddition between pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), seen in 2.1.1.2 (Scheme 28).



Scheme 28. Polyaddition between ODA and PMDA forming polyamic-acid.

The resulting polyamic-acid, poly[*N*,*N'*-bis(phenoxyphenyl)-pyromellitamic acid] were cured on copper wires, forming PI via ring-closure imidization (Scheme 29). It is important to clarify that no cross-link reaction takes place at this stage since no reactive sites are present on chain backbones. PIs are not cross-linked polymers.



Scheme 29. Formation of polyimide after the imidization step.

The generic procedure, adopted in this work, for the synthesis of polyamic-acids is described herein.

In a 2 L five-necked round bottom glass vessel, equipped with a mechanical stirrer and a thermocouple, solvent (NMP, Cyrene or NFM) and oxydianiline are added at room temperature and the stirrer is turned on. The mixture is stirred and small portions of pyromellitic dianhydride are added over an interval of at least 15 minutes while monitoring the temperature, which is maintained below 60°C to avoid premature imidization and precipitation of the polymer. PMDA is added until the viscosity reaches a value between 55000 and 65000 cPs (9 grams of resin are mixed with 1 gram of solvent before the measurement). The PMDA-ODA molar ratio must not exceed 1:1. Once the target viscosity is reached, the mass is kept under stirring for 4 hours at 30°C to bring the reaction to equilibrium. At the end, thinners as xylene or naphthas are added to bring the viscosity to a range between 1000 – 2000 cPs in order to make the resin able to be applied and cured on copper wires. Resulted resins are filtered and, if possible, cured by the horizontal enameler oven "MAG HEL4/5" owned by Elantas Europe S.r.l. and subjected to mechanical, electrical and thermal tests (see chapter 1.4). Liquid resins are characterized by GPC and IR spectroscopy.

First, a generic synthesis of a PAA in NMP is performed in order to compare characteristics of liquid and cured resin to those ones of PAAs made in alternative solvents. Batch EL43 is considered as PAA reference. The solvent NFM was not used due to low availability in the company.

4.2.1. Synthesis and Characterization of PAA in NMP

PAA in NMP was synthetized according to the generic synthesis described before. At the end of the synthesis, the resin was diluted, filtered and applied by the enameling oven. Synthesis parameters and characteristics of the liquid resin are showed below.

Table 18. Synthesis parameters and characteristics of the liquid resin.

Batch	*Solvent*	*Monomers [wt%]*	*Molar ratio [MDA-PMDA]*	*η [cPs]*[a]	*S.C. [%]*[a]	*Appearance*
EL43	NMP	32.3	1 - 0.97	2460	19.5	good

[a] *Measured after the dilution.*

Mw Mn and polydispersion index are showed herein.

Table 19. Molecular weight distribution values obtained by GPC.

Batch	*Mw*	*Mn*	*Mw/Mn*
EL43	57597	32712	1.76

Characteristics of cured resins and results of tests conducted on enameled copper wires are reported herein.

Table 20. Characteristics of cured resin.

	Film aspect	*Wire aspect*	*Jerk test*	*Flexibility [%]*	*Cut-through [°C]*	*Tgδ [°C]*
EL43	good	good	passed	25	>550	280

GPC conducted on liquid sample of EL43 is depicted below:

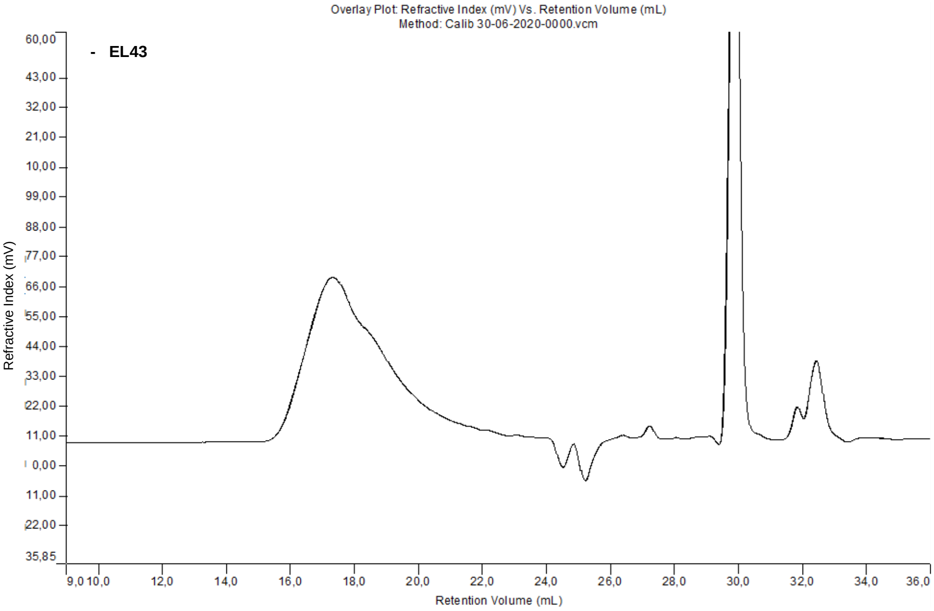


Figure 41. GPC chromatogram of PAA in NMP (EL43).

FT-IR spectroscopy was conducted on liquid resin and cured wire and are reported below:

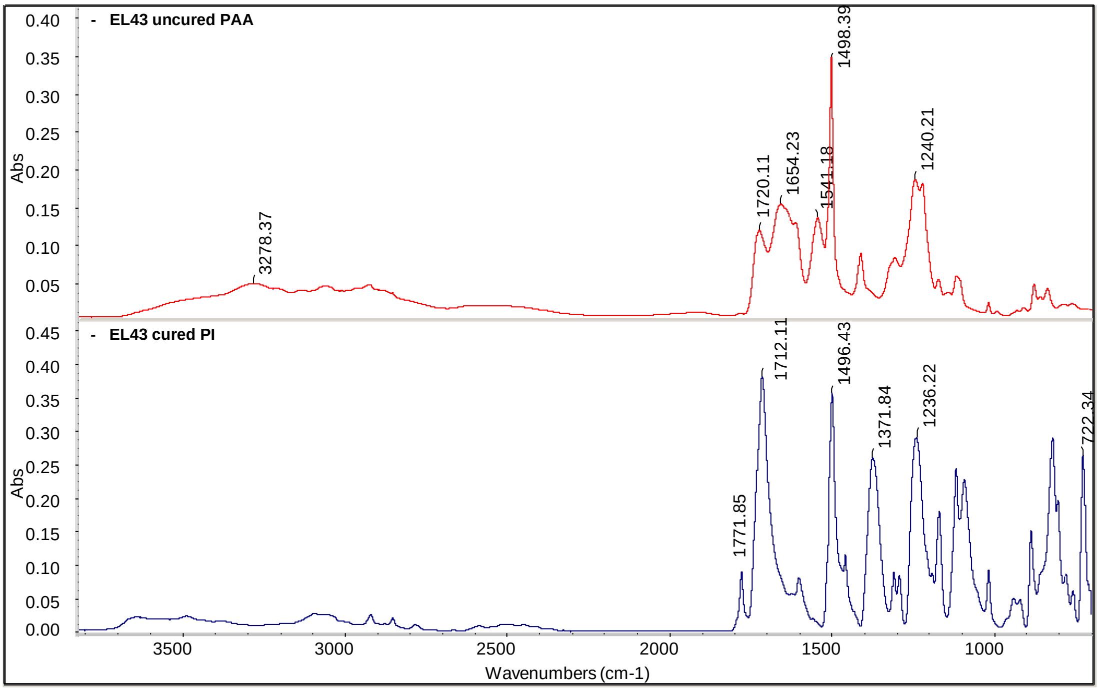


Figure 42. FT-IR spectra of uncured NMP-based PAA (top) and its cured form, PI (bottom).

It shows important differences between uncured PAA and cured PI that are explained in chapter 2.1.2.

4.2.2. Synthesis and Characterization of PAA in Cyrene

It was seen that the hansen solubility parameters of cyrene are very far from those of PAA acid. Despite low expectation of success, it was decided to try to synthetize a PAA with Cyrene as reaction medium following the standard diisocyanate route. Only one attempt was made due to low amount of solvent available.

4.2.2.1. Results and Discussion

Table 21. Synthesis parameters and characteristics of the liquid resins.

Batch	*Solvent*	*Monomers [wt%]*	*Molar ratio (MDA-PMDA)*	*η [cPs]*	*S.C. [%]*	*Appearance*
SG881	CYR	32.0	1:0.80	-	-	turbid

Table 22. Characteristics of the cured resin

	Film aspect	*Wire aspect*	*Jerk test*	*Flexibility [%]*	*Cut-through [°C]*	*Tgδ [°C]*
SG881	bad	-	-	-	-	-

As expected, after 5 hours of reaction, the mixture remained turbid and the viscosity did not grow, a sign that the polymerization stopped at early stages due to low reactivity of the reaction mixture. GPC was not performed to avoid problems during the analysis due to the high concentration of monomers and oligomers in the sample.

Due to low amount of solvent available and also because of very high probability of failure, it was decided to not try with other attempts.

4.2.3. Synthesis and Characterization of PAA in MDPA

MDPA was used as reaction medium for the synthesis of polyamic-acids. The generic procedure was followed and NMP was replaced with MDPA. Attempts are summarized below with the reference batch (EL043).

Table 23. Synthesis parameters and characteristics of the liquid resins.

Batch	*Solvent*	*Monomers [wt%]*	*Molar ratio [MDA-PMDA]*	*η [cPs]*[a]	*S.C. [%]*[a]	*Appearance*
EL43	**NMP**	**32.3**	**1-0.97**	**2460**	**19.5**	**good**
EL45	MDPA:XIL	20.6	1-0.96	2120	12.4	good
EL46	MDPA	21.0	1-0.97	648	18.6	good
EL48	MDPA	25.8	1-0.97	2000	18.2	good
EL50	MDPA	22.7	1-0.99	1590	11.0	good
SG818	MDPA	16.8	1-0.99	2050	11.1	good

[a] *Measured after the dilution.*

Mw Mn and polydispersion index are showed herein.

Table 24. Molecular weight distribution values obtained by GPC.

Batch	*Mw*	*Mn*	*Mw/Mn*
EL43	57597	32712	1.76
EL45	79188	45970	1.75
EL46	31904	18195	1.75
EL48	55356	31981	1.73
EL50	141314	86287	1.64
SG818	116815	74098	1.58

Performed tests and results of the enameled copper wire are reported herein:

Table 25. Characteristics of cured resins.

Batch	*Film aspect*	*Wire aspect*	*Jerk test*	*Flexibility [%]*	*Cut-through [°C]*	*Tgδ [°C]*
EL43	good	good	passed	25	>550	280
EL45	good	good	failed	0	>550	248
EL46	good	good	failed	0	>550	255
EL48	good	good	failed	0	>550	268
EL50	good	good	failed	0	>550	251
SG818	good	good	passed	25	>550	280

Solvent-based polyamic-acids exhibit higher viscosity compared to other polymers due to their high degree of polymerization. In order to have a good processability, they must be significantly diluted, lowering the solid content. This property is undesired in wire enamels because it implies that a larger quantity of solvent has to be removed during the enameling process and, in general, a low solid content varnish leaves thin coatings on the wire, making necessary more material to reach desired enamelled wire thickness. In this context, in EL45, xylene was added at the beginning of the reaction to obtain a reaction mass less viscous and more workable. EL48, EL50 and SG818 were synthetized only using MDPA as reaction medium and changing monomer wt.% and molar ration between monomers. All the batches, except SG818, were diluted with xylene as thinner to bring the viscosities to a range between 1000 – 2000 cPs in order to make the resins able to be applied and cured on copper wires. SG818 was not diluted as its viscosity was already low due to its low dry content.

GPCs were conducted on liquid samples and compared with the reference.

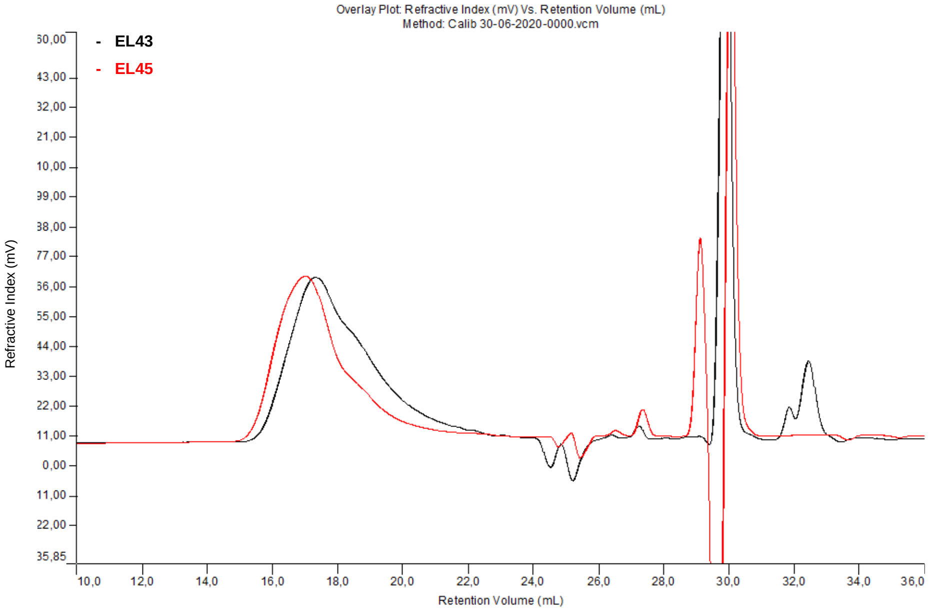


Figure 43. Superimposed GPC chromatograms of EL43 with EL45

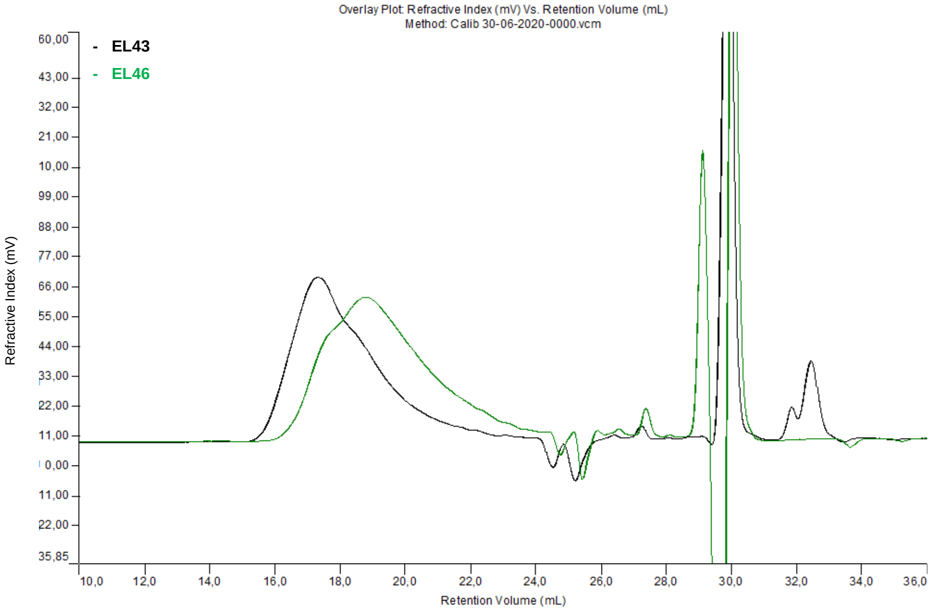


Figure 44. Superimposed GPC chromatograms of EL43 with EL46.

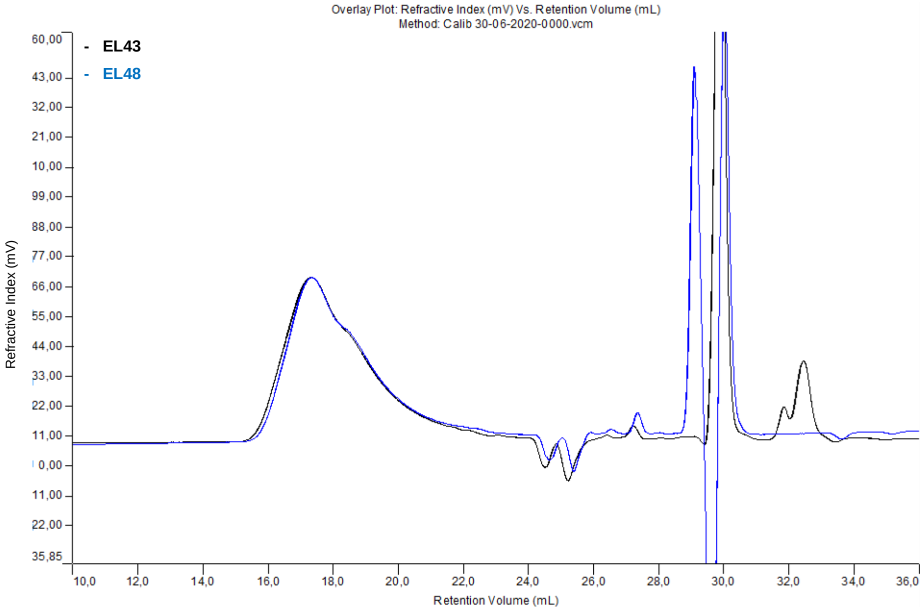


Figure 45. Superimposed GPC chromatograms of EL43 with EL48.

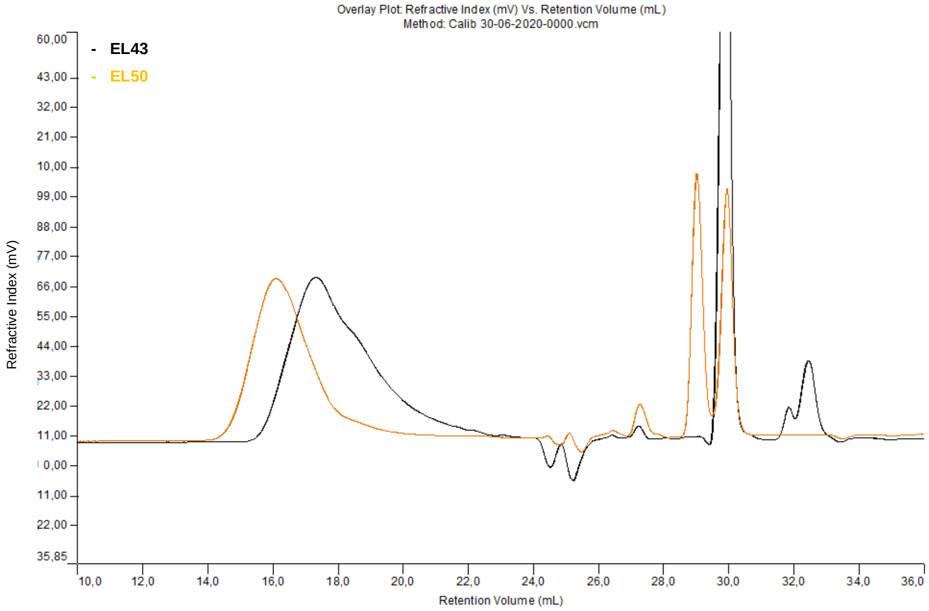


Figure 46. Superimposed GPC chromatograms of EL43 with EL50.

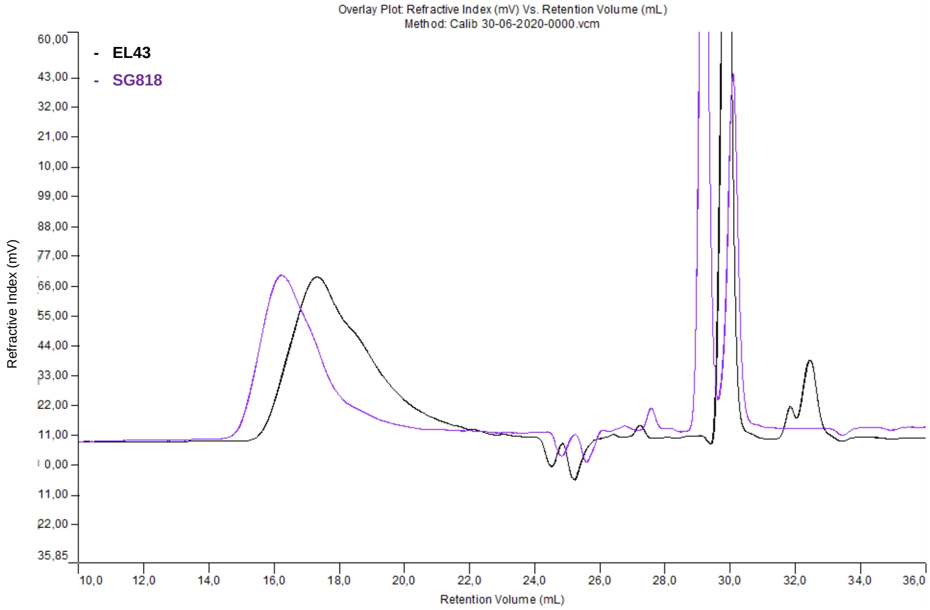


Figure 47. Superimposed GPC chromatograms of EL43 with SG818.

ATR spectra between cured wire enamels of PI reference (EL43), EL50 (jerk test failed) and SG818 (jerk test passed) are compared below.

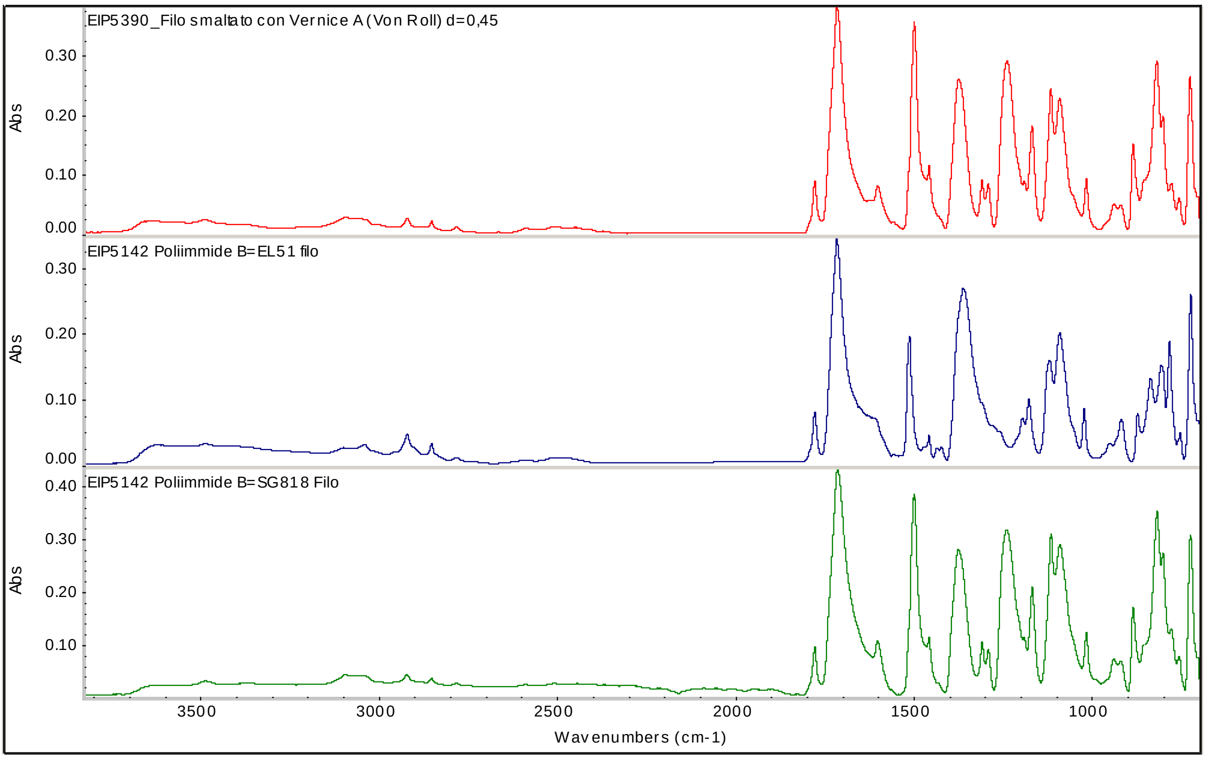


Figure 48. Comparison between ATR spectra of the reference PI enamel (red), EL51, and SG818.

4.2.4. Discussion

Except for the batch EL43, it is noticeable that molecular weight distributions of PAAs made in MDPA are comparable or even higher than the reference (batch EL43). Anyway, only batch SG818 passed the jerk test and obtained a high Tgδ, an indication to the fact that polyamic-acids made in MDPA have to reach a molecular weight distribution much higher than polyamic-acids made in NMP, in order to achieve comparable mechanical characteristics in the resulting polyimide enamel. In addition, SG818 was the only batch to be diluted with MDPA and not with lower boiling solvents (xylene, naphthas). This could be an indication that the co-solvent may have caused problems during the wire enameling phase, resulting in morphological irregularity in the obtained PI that caused the jerk test to fail, despite higher molecular weight of the polymer, such as with batch EL50 as example.

FT-IR spectroscopies conducted on cured enamels does not shows substantial differences between the reference PI EL43 and the NMP-free SG818 which obtained similar performances to standard PIs. On the other hand, EL51 show a less intense band at 1500 cm^{-1} and, in particular, the total absence of that one at around 1370 cm^{-1}, an indication that the imidization step did not proceed as usual.

4.3. Conclusions

The aim of this project was to synthetize NMP-free polyamide-imides and polyimides wire enamel.

A first study was conducted using the Hansen solubility parameter software (HSPiP™) in order to choice solvents with solubility parameters as close as possible to those of NMP. Three solvent were chosen to carry out syntheses: dihydrolevoglucosenone (commercial name Cyrene), *N*-formylmorpholine (NFM) and 3-methoxy-*N*,*N*-dimethylpropionamide (MDPA). The latter was only used for the synthesis of polyimides as it is already reported in the literature for its use in polyamide-imides. Resulting PAIs and PAAs were then applied and cured on copper wires. Unfortunately, Cyrene turned out to be a bad solvent for both PAI and PAA (PI precursor), and a commercial application would be nearly impossible. For this reason, Cyrene has been put aside.

The solvent NFM was investigated only for the synthesis of polyamide-imides due to low availability of PMDA. It was able to synthetize a PAI with a good film aspect but it was not possible to obtain a molecular weight high enough to guarantee good mechanical characteristics of the cured enamel, i.e. all the jerk tests failed. Even if the obtained results were not satisfying, NFM-based PAI could be promising for applications were the use of NMP is strictly banned; i.e., in food-contact manufactures.

The best results were obtained from MDPA. The resulting enameled wires achieved good mechanical, thermal and electrical characteristics that are comparable to standard PIs. Attempts to introduce lower boiling point thinners in the mixture to decrease its viscosity were not successful due to poor mechanical characteristics of the resulting cured PI.

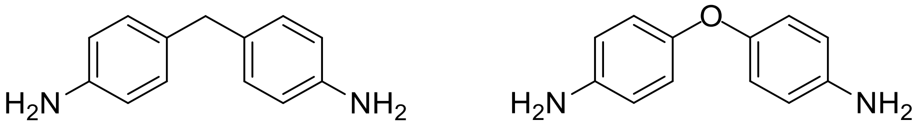
5. Bio-based Wire Enamels

Due to growing concerns regarding environmental sustainability, strongly driven by expanding and demanding ecological regulations, renewable resources are increasingly receiving both industrial and academic attention.[192-194] Among renewable sources for the synthesis of polymers, vegetable oils are generally considered the most important class due to their availability and versatility. Vegetable oils are used to synthetize different types of polymers such as polyurethanes, polyethers, polyesters, polyamides, polyimides, polycarbonates, and polyolefins.[195-196] The variety of applications range from paints, adhesives to composites and biomedical applications.[194] Different thermosetting and thermoplastic polymers can be obtained with various characteristics to meet the most diverse industrial needs, thus confirming the potential of vegetable oil-based polymers as alternatives to petroleum-based ones.[197-198] Vegetable oils are made of different triglycerides which are the esterification products of glycerol with various fatty acids. The heterogeneity and variability of the triglycerides, which is due to the statistical distribution of fatty acids per triglyceride, makes difficult to reproduce a correlation between the material property and the monomer structure. However, using difunctional fatty acid-based monomers such as diols, diacid and diamines with a well-defined chemical structure can lead to bio-based polymers with better tunable properties.[199-200]

Fatty dimers have been used in the past to prepare polymers with novel molecular architectures, such as PU-acrylate coatings, reversible ionic interaction, and hydrogen bonded supramolecular polymers.[201-203] They are reportedly used to induce phase segregation, suppress H-bonding and regulate crystallinity, viscosity and thermomechanical properties in renewable polyurethanes, polyamides, polyimides and their bio-composites.[204-208]

In the wire enamel area, among all, the most interesting fatty acid derivatives are bio-based diamines as they could replace aromatic diamines such as 4,4’-oxydianiline (ODA) and 4,4’-methylenedianiline (MDA) (Scheme 30), used for the synthesis of polyimides and polyester-imides respectively.

18 **20**



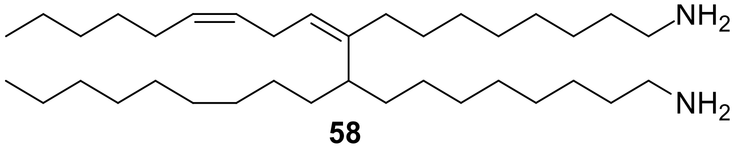
4,4'-methylenedianiline 4,4'-oxydianiline

Scheme 30. Most used diamines for the production of polyester-imides and polyimides.

Aromatic diamines, in addition to being petroleum-based, are of health and environmental concern. They are considered potential occupational carcinogens by the US National Institute for Occupational Safety and Health which has set a permissible exposure limit at 0.01 ppm over an eight-hour time-weighted average, and a short-term exposure limit at 0.10 ppm since they are suspected carcinogen.[209-210] In addition, MDA, is included in the "substances of very high concern" list of the European Chemicals Agency (ECHA).[211]

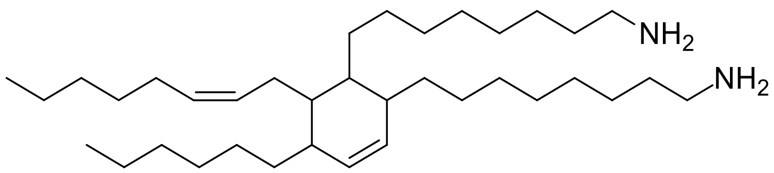
Possible alternatives could be long-chain aliphatic diamines deriving from dimerized fatty acids of vegetable oils.

For the present work, high purity, with 100% renewable carbon bio-based diamines were used. Mentioned diamines, in the terms of chemical structure are amine derivatives of dimerized fatty acids obtained from vegetable oils (e.g. soybean oil) by chemical conversion. Examples of possible structures (acyclic, cyclic and aromatic) of mentioned bio-based diamines are presented in Scheme 31.[212]



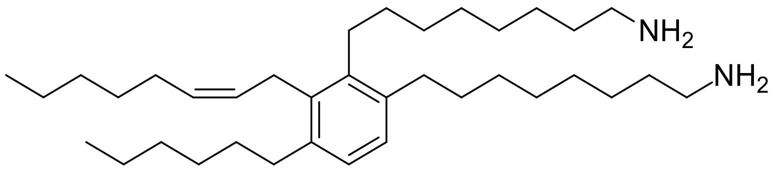
58

acyclic dimer diamine



59

cyclic dimer diamine



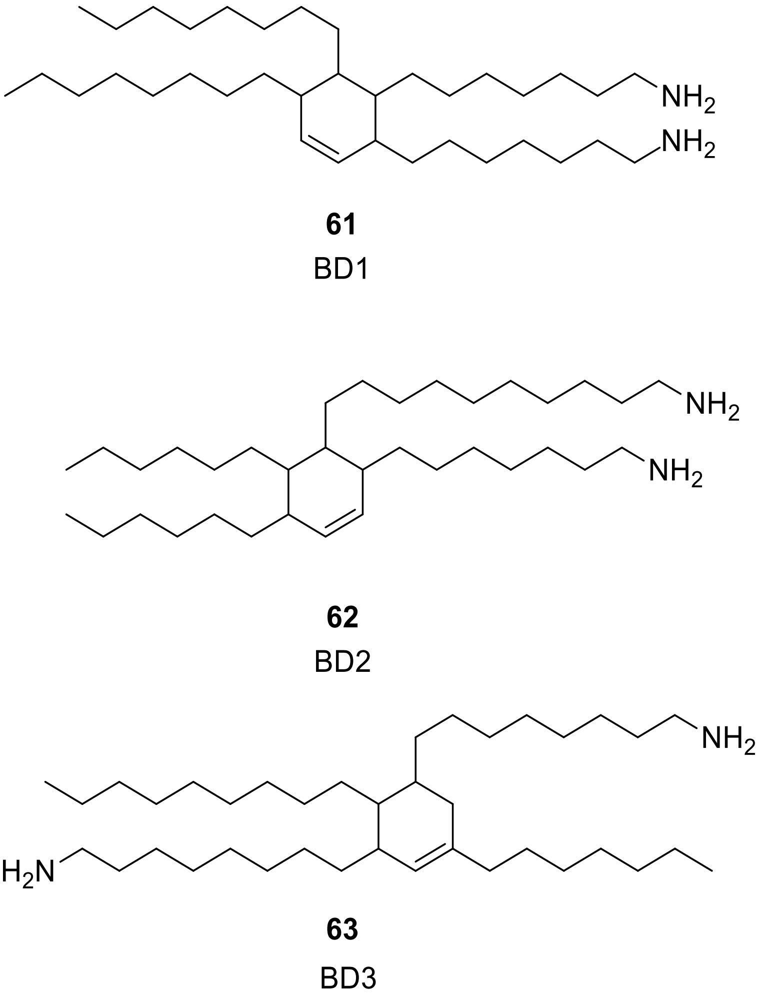
60

aromatic dimer diamine

Scheme 31. Possible chemical structure of amine derivative of dimerized fatty acids.

Mentioned bio-based fatty dimer diamines with long alkyl branches are named BD1, BD2 and BD3 were reported in the literature as useful building blocks to develop room temperature self-healing polyimides with high mechanical properties and curing agents for epoxy systems.[213-214] However, applications of fatty diamine in the synthesis of PIs and PEIs as wire enamels have not yet been evaluated.

In view of these convincing aspects, it was decided to synthetize polyimide precursor and polyester-imide wire enamels by using bio-based diamines instead of oxydianiline and methylenedianiline. Chemical structure and molecular weight distribution of obtained liquid enamels were investigated. The resins were then applied and cured on copper wires and evaluated in terms of mechanical, electrical, and thermal properties. Predicted structures of bio-based diamines (BD1, BD2, BD3) used in the present work are presented in Scheme 32.[215]



61
BD1

62
BD2

63
BD3

Scheme 32. Possible chemical structure of bio-based diamines used.

These amines are a di-functional derivative of C_{18} fatty acids resulting from dimerization or/and trimerization process. Consequently, they contain 100% renewable carbon. These structures could bring flexibility to the resulting PIs and PEIs but, on the other hand, they could also lower thermal stability of wire enamels.

Amine content of each bio-based diamine was checked with acid-base titration. The equivalent weight (E.W.) of the diamines was determined through a classical acid-base titration, method typically used for the quality check of amines. Functionality is then calculated by dividing molecular weight (M.W.) by equivalent weight (E.W.). The amine’s molecular weight was given by the producer and confirmed with the literature.[215]

Table 26. Amine content of each reagent.

Amine	*M.W. [g/mol]*[a]	*E.W. [g/eq]*	*Functionality*
BD1	581.9 ± 2.1	270.1	2.2
BD2	587.0 ± 6.1	278.4	2.1
BD3	550.2 ±1.0	275.0	2.0

[a] *Values are obtained from Blazek et al.*[215]

NMR and FT-IR spectra were conducted and are in accordance with the literature.[215-218]

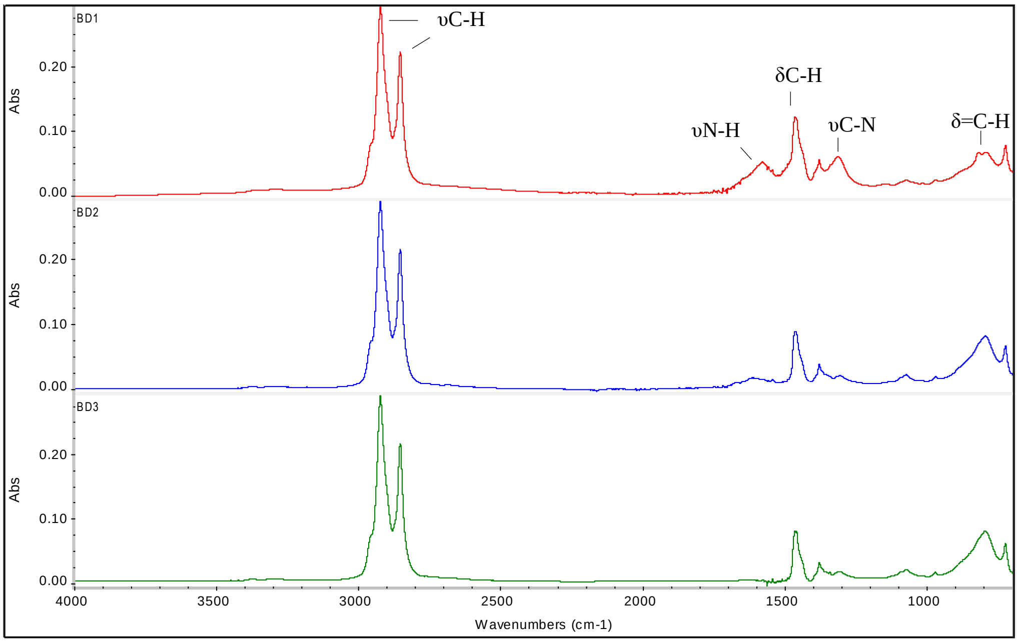


Figure 49. FT-IR spectra of BD1 (red), BD2 (blue), BD3 (green)

- Compound **61**

^{1}H-NMR: (500 MHz, $CDCl_3$) δ_H = 6.89 – 6.76 (m), 5.34 – 5.05 (m), 2.64 – 2.62 (t), 2.50 (s, broad), 1.93 (s, broad), 1.39 – 1.38 (m), 1.25 – 1.22 (m), 0.86 – 0.79 (m).

- Compound **62**

^{1}H-NMR: (500 MHz, $CDCl_3$) δ_H = 6.96 – 6.95 (m), 5.32 – 5.03 (m), 3.28 – 3.26 (t), 2.62 – 2.59 (t), 2.47 (s, broad), 1.91 (s, broad), 1.37 (m), 1.22 – 1.20 (m), 0.93 – 0.77 (m).

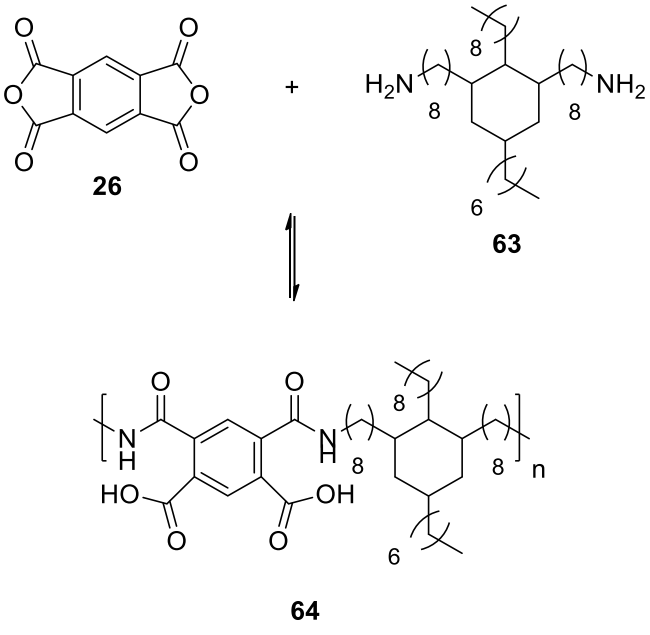
- Compound **63**

^{1}H NMR: (500 MHz, $CDCl_3$) δ_H = 6.99 – 6.75 (m), 5.33 – 5.04 (m), 2.64 – 2.61 (t), 2.49 (s, broad), 1.93 (s, broad), 1.40 – 1.37 (m), 1.24 – 1.22 (m), 0.85 – 0.79 (m).

5.1. Bio-based Polyimides

5.1.1. Synthesis and Characterization

Polyamide-imides precursor, hence polyamic-acids were synthetized following the standard approach (see chapter 2.1.2.2) which involves a polyaddition between pyromellitic dianhydride and bio-based diamine (BD1, BD2 and BD3) in NMP as reaction medium: bio-based diamines were added slowly to the mixture of NMP and PMDA until reaching the equimolar amount. The reactions were left under stirring for 5 hours after the addition of the amines and then they were stopped. GPC and IR spectroscopy were carried out on liquid samples. Equimolar amount of diamine and dianhydride was used in all batches. Reaction temperature was always kept below 60°C to avoid premature imidization of the polymer and consequent precipitation. The formation of polyamic-acid is schematized below (Scheme 33).

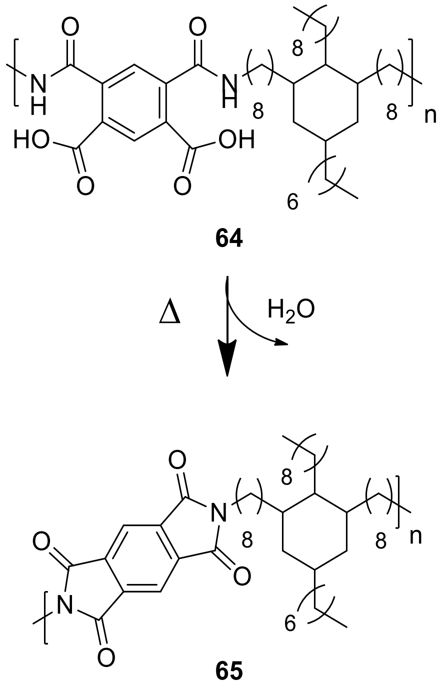


Scheme 33. Polyamic-acid formation.

Table 27. Entry list.

Batch	*Amine*	*Anhydride*
REFERENCE	**ODA** (**20**)	**PMDA** (**26**)
EL85	BD2 (**63**)	PMDA (**26**)
EL90	BD3 (**62**)	PMDA (**26**)
EL97	BD1 (**61**)	PMDA (**26**)

Synthetized PAA resins were characterized via GPC and IR spectroscopy and then applied on copper wires where the imidization step via ring closure is performed at high temperature in the enameling oven, giving cured PI enameled copper wires (Scheme 34).



Scheme 34. Thermal imidization step.

GPC overlaps between batches EL85 (red), EL90 (blue), EL97 (green) and a commercial PAA reference (black) are reported as follows.

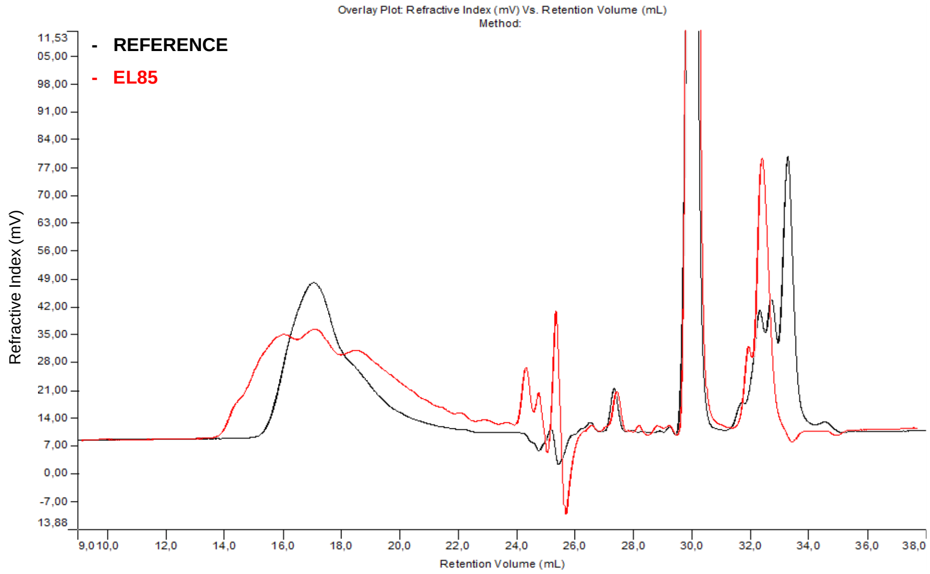


Figure 50. Superimposed GPC chromatograms of batch EL85 (red) with reference batch EL43 (black).

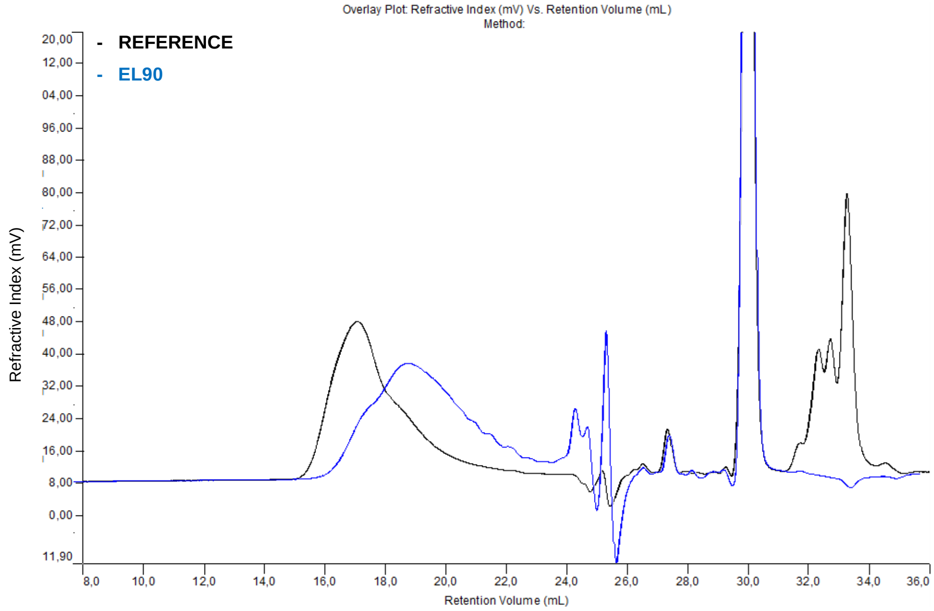


Figure 51. Superimposed GPC chromatograms of batch EL90 (blue) with reference batch EL43 (black).

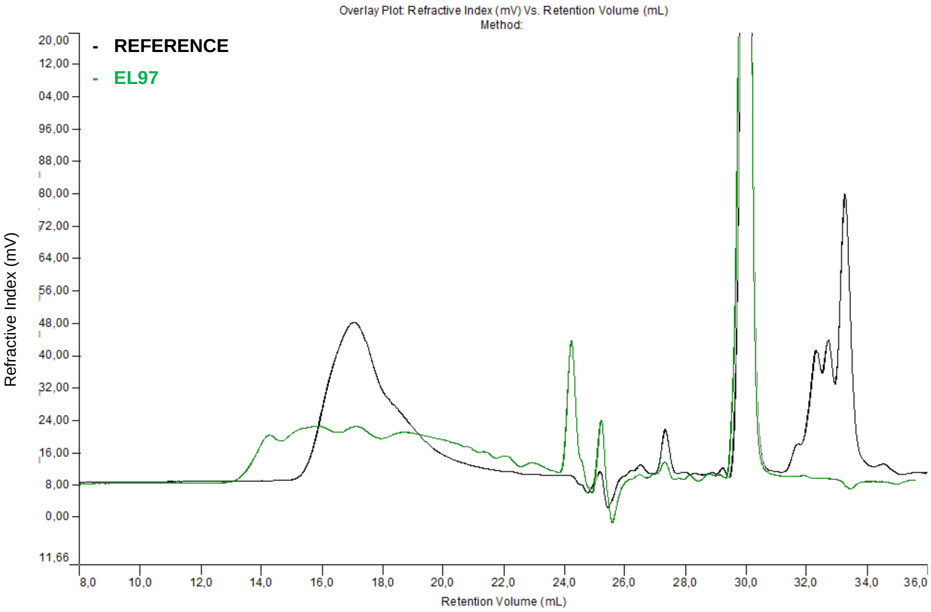


Figure 52. Superimposed GPC chromatograms of batch EL97 (green) with reference batch EL43 (black).

FT-IR spectra of cured PI enamels were compared with the commercial PI enamel (reference, red) and reported here (Figure 53).

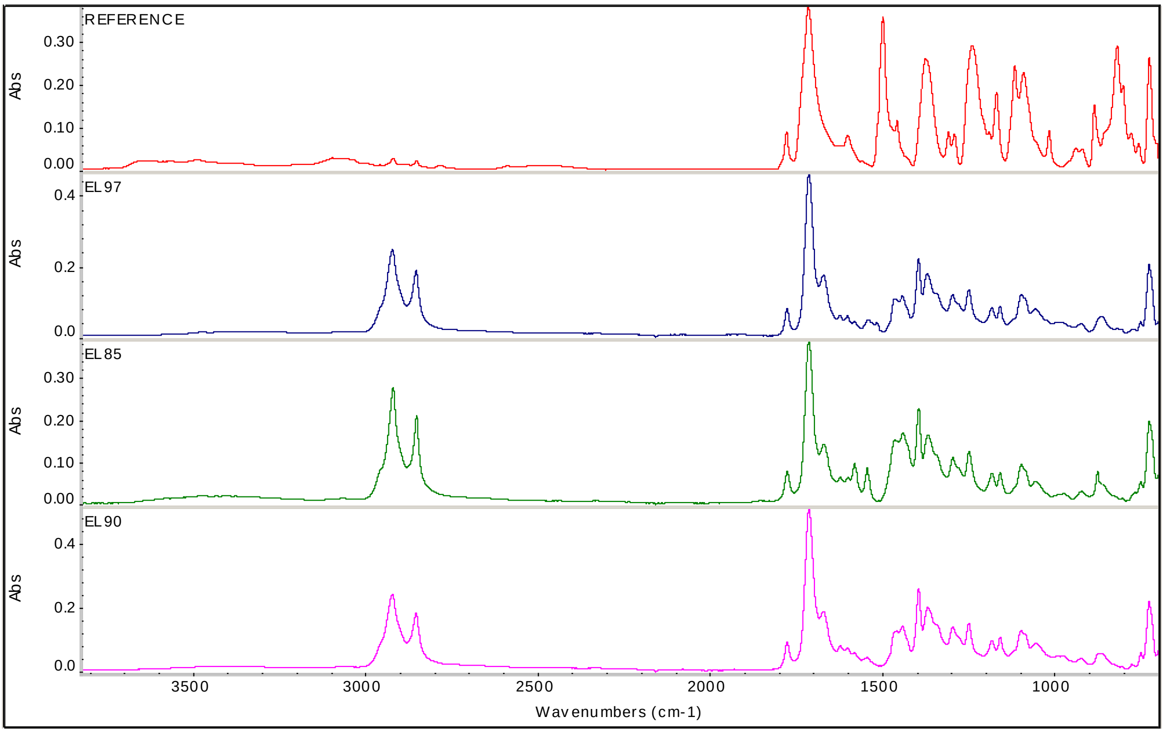


Figure 53.FT-IR spectra of cured PIs: reference (red), EL97 (blue), EL85 (green), EL90 (purple).

Thermo-mechanical and electrical properties of cured enameled wires were evaluated and compared with a commercial PI (Table 30).

5.1.2. Results and Discussions

Table 28. Synthesis parameters and characteristics of the liquid resins.

Batch	*Amine*	*Monomer [%]*	*η [cPs]*	*S.C. [%]*	*Appearance*
REFERENCE	**ODA**	**32.3**	**2460**	**19.5**	**clear**
EL85	BD2	24.1	1100	21.5	clear
EL90	BD3	34.4	1800	33.5	clear
EL97	BD1	25.0	1130	25.1	clear

Table 29. Molecular weight distribution values obtained by GPC.

Batch	*Mw [g/mol]*	*Mn [g/mol]*	*Mw/Mn*
REFERENCE	**57597**	**32712**	**1.76**
EL85	87232	28059	3.11
EL90	28203	17068	1.65
EL97	106088	21031	5.04

Table 30. Characteristics of cured resins.

Batch	*Film aspect*	*Wire aspect*	*Jerk test*	*Flexibility [%]*	*Cut-through [°C]*	*Tgδ [°C]*
REFERENCE	**good**	**good**	**passed**	**25**	**>550**	**280**
EL85	good	good	passed	30	420	191
EL90	good	good	passed	30	310	170
EL97	good	good	passed	30	390	38

FT-IR spectra of EL85, EL90 and EL97 are almost equal to each other. They show characteristic bands of polyimide at 1770, 1712, 1370 and 722 cm^{-1}, confirming the successful synthesis of polyimides. The medium bands at 2850 and 2940 cm^{-1} are related to the C-H stretching absorption of the aliphatic moiety, absent in the reference sample.

It is immediately evident that the thermal and electrical characteristics of all the enameled are way lower than the reference batch EL43. These results come from the fact that the molecular structures of the bio-based amines are aliphatic and, unlike the aromatic ones, have lower thermal and electrical characteristics. On the other hand, mechanical characteristics such as flexibility and jerk test resistance, are way higher. No improvements were seen in batches with a higher degree of polymerization (batch EL97).

These results do not allow these materials to be used as wire enamels due to their low thermal property, but they could be used in other fields where high thermal characteristics are not required but rather a higher level of safety and good mechanical characteristics.

5.2. Bio-based Polyester-imides

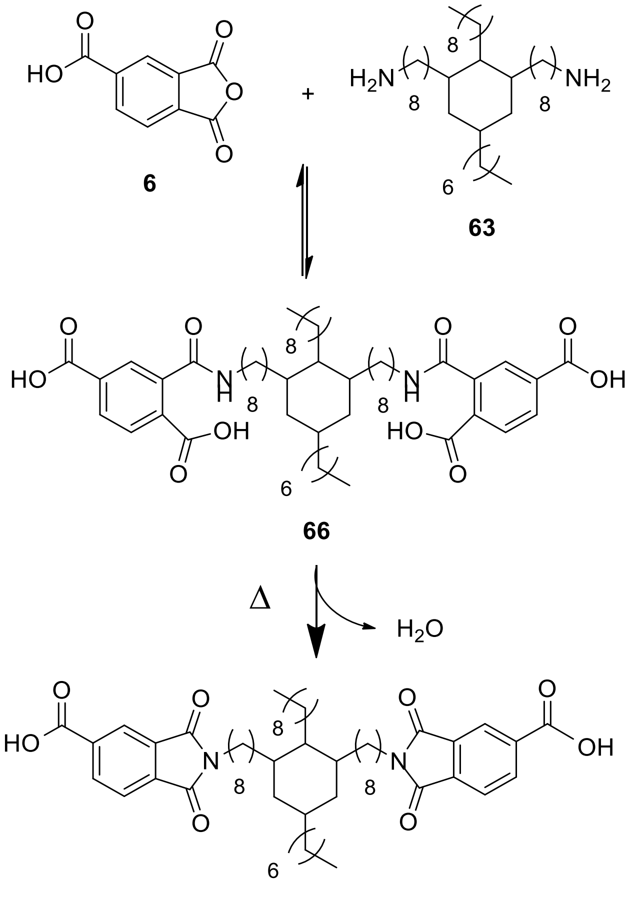
5.2.1. Synthesis and Characterization

Bio-based amines BD1, BD2 and BD3 were used to synthetize 3 batches of polyester-imide by replacing the total amount of 4,4'-methylenedianiline (MDA), leaving the synthesis process unchanged. Equimolar amount between diamines and carboxylic diacids was always used.

Table 31. Entry list.

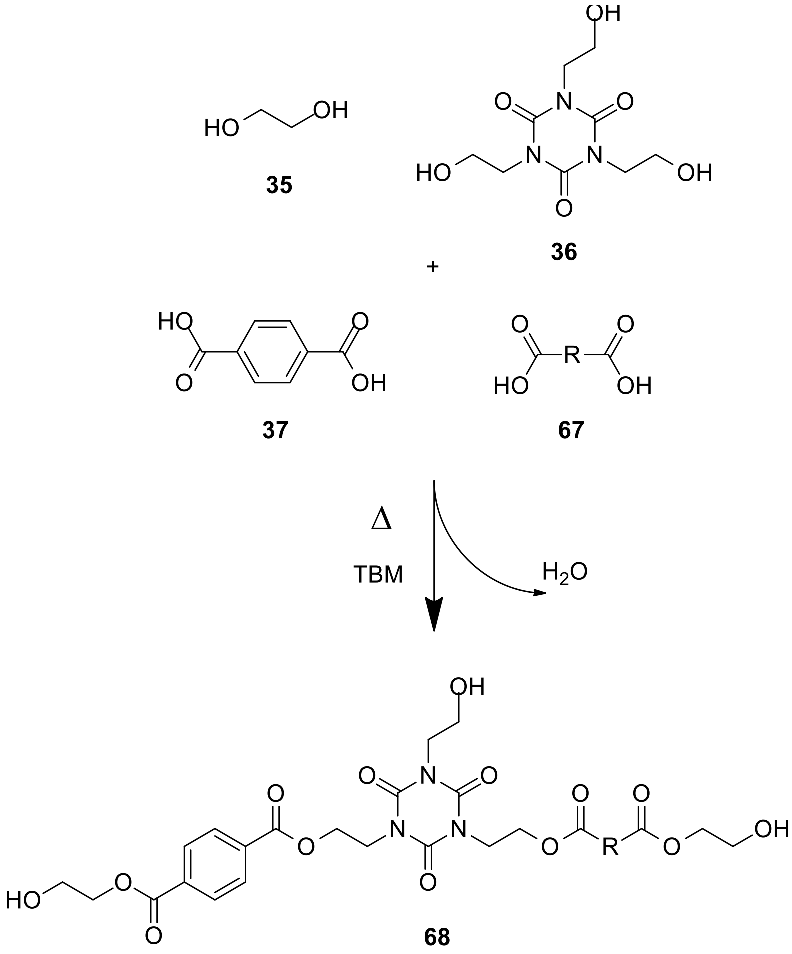
Batch	*Amine*	*Carboxilic acids*	*Alcohols*
REFERENCE	**MDA** (**2**)	**TMA** (**6**), **TPA** (**37**)	**MEG** (**35**), **THEIC** (**36**)
EL92	BD3 (**63**)	TMA (**6**), TPA (**37**)	MEG (**35**), THEIC (**36**)
EL93	BD3 (**63**)	TMA (**6**), TPA (**37**)	MEG (**35**), THEIC (**36**)
EL95	BD2 (**62**)	TMA (**6**), TPA (**37**)	MEG (**35**), THEIC (**36**)
EL96	BD1 (**61**)	TMA (**6**), TPA (**37**)	MEG (**35**), THEIC (**36**)

PEIs were synthetized following the process described herein. In a 2 L five-necked round bottom glass vessel, equipped with a mechanical stirrer, a thermocouple, a Vigreux column and a distillation apparatus, an excess of ethylene glycol was added. The reaction is run in an excess of ethylene glycol as medium, which is eventually removed during the transesterification step. The mass was stirred and heated to 125°C and once the temperature was reached, THEIC, terephthalic acid and tetrabutyl titanate (TBM) were added and the mixture heated to 135°C. At this temperature, trimellitic anhydride is added and the mass heated to 150°C. The bio-based diamine was then added stepwise. the mass was progressively heated to 210°C. At this condition, amines react toward anhydrides via polyamic-acid step and subsequent thermal imidization with release of water which is distilled off to shift the reaction equilibrium to the products (Scheme 35). The result is the diimide diacid **67**.



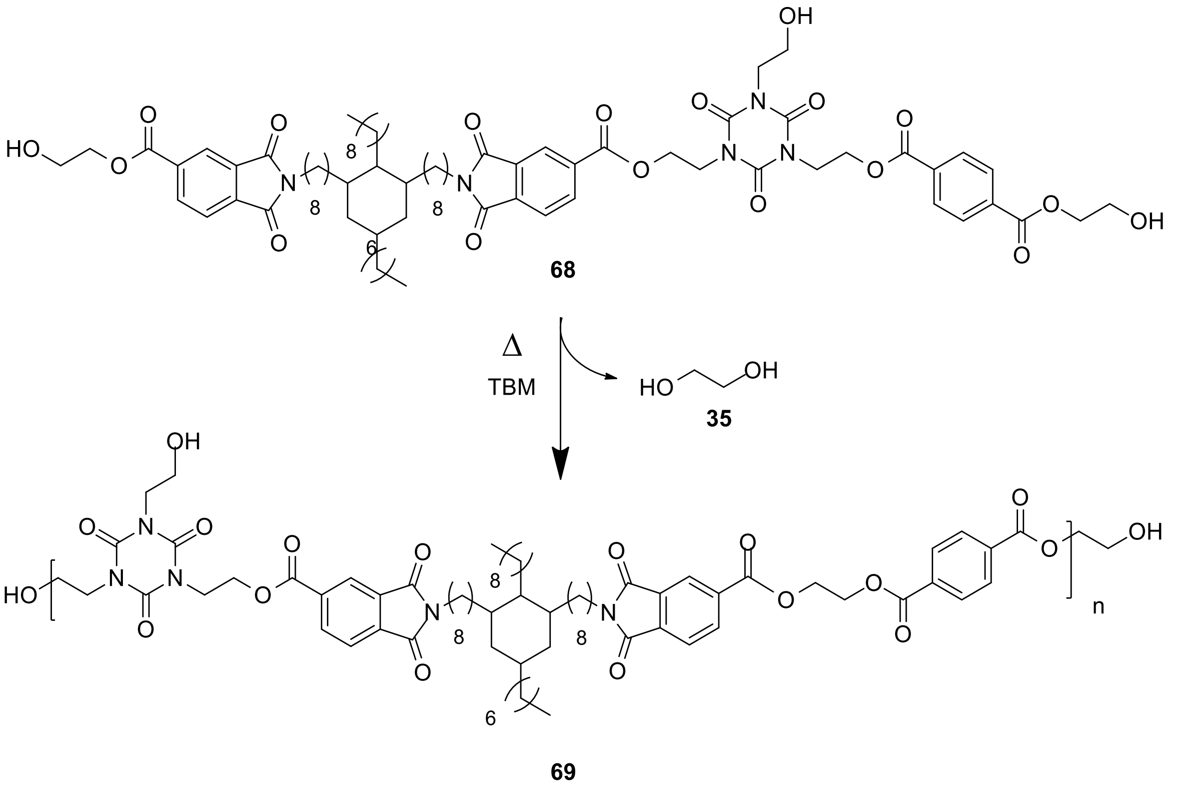
Scheme 35. Thermal imidization step and formation of the DIDA.

At the same time, ethylene glycol and THEIC react toward carboxylic acids of **37** and **67** giving ester intermediates and oligomers as **68**, while water is distilled off (Scheme 36).



Scheme 36. Esterification step.

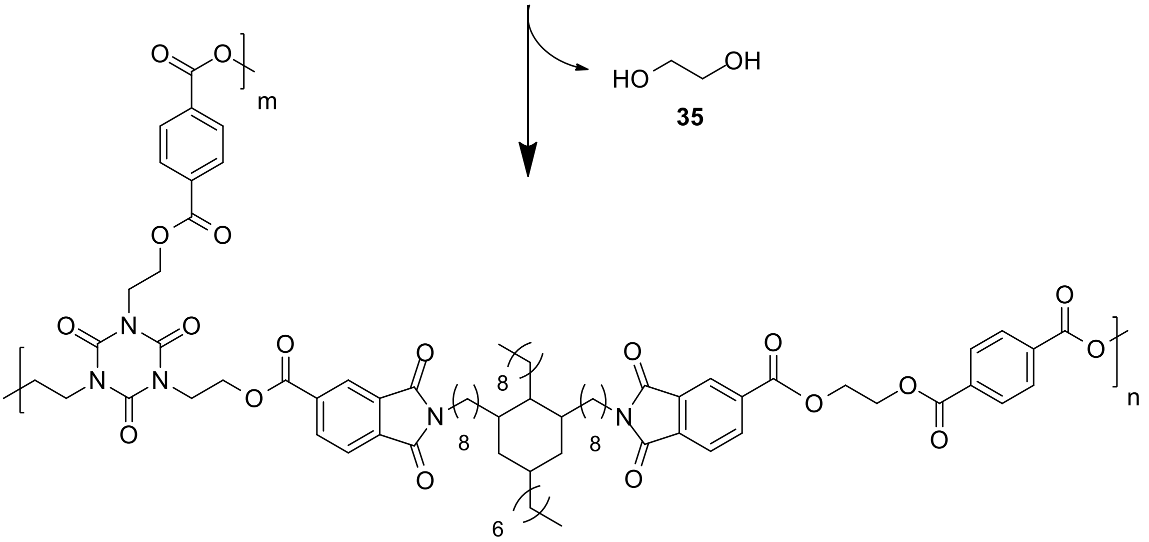
Conditions were maintained still until the overhead column temperature begin to drop, indicating that the condensation water has been completely distilled off. When the overhead column temperature dropped to 80°C, the temperature was set to 220°C, the vacuum pump was connected and set to operate at 100 mBar. These conditions allow transesterification between ester oligomers by elimination of ethylene glycol and molecular weight of the polyester-imide begin to increase. (Scheme 37).



Scheme 37. Transesterification step.

At this step, reactions were controlled via GPC. The condensation step was ended when molecular weight of the polymers equaled or exceeded that of the standard PEI. At this point, the vacuum pump and the heater were turned off, cresylic mixture and thinners were added to adjust viscosity of the mass. The final products were characterized via GPC and IR spectroscopy. The resulting resins were then applied on copper wires where additional inter-chain transesterifications (cross-links) occurred in the enameling oven at around 500°C, giving cured PEI enameled copper wires (**70**) Scheme 38. Cross-linking during the curing step.(Scheme 38). Mechanical, thermal, and electrical properties were then evaluated.

69



70

Scheme 38. Cross-linking during the curing step.

The first batch (EL92) was repeated and the molecular weight increased in order to see if this property can improve thermal and electrical performances of the final product.

GPC overlaps between batches EL92 (orange) EL93 (red), EL95 (blue), EL96 (green) with a commercial PEI (black) are reported as follows.

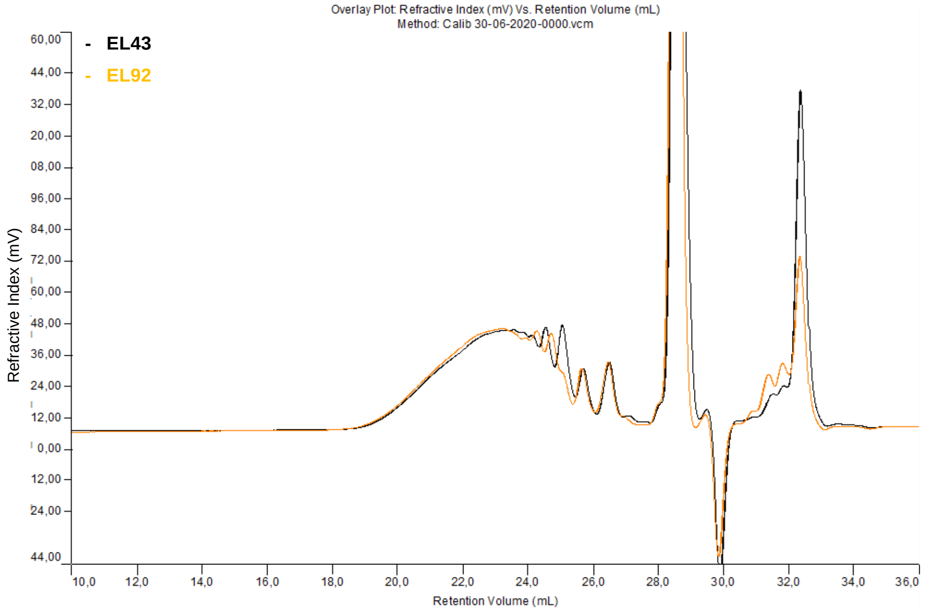


Figure 54. Superimposed GPC chromatograms of batch EL92 (orange) with the PEI reference (black).

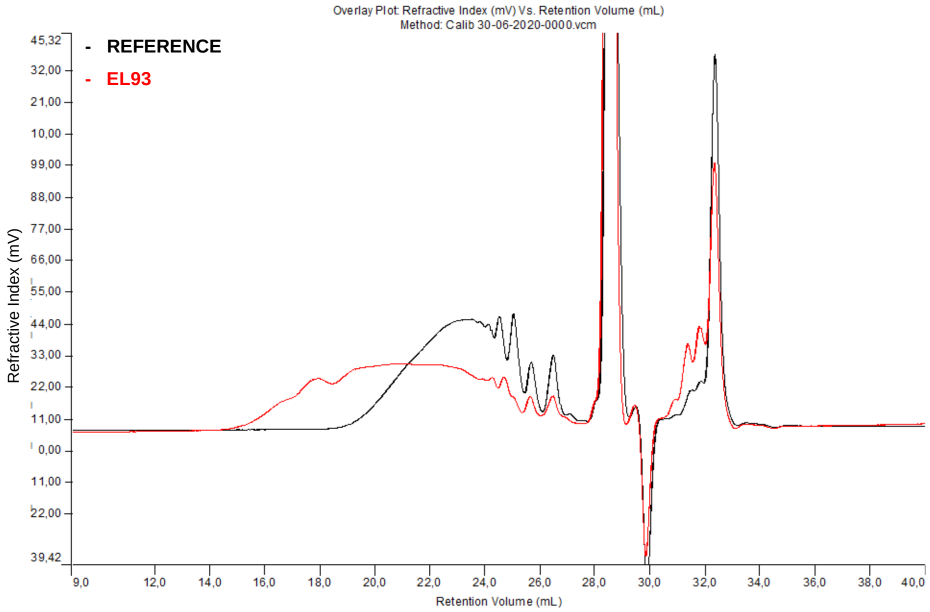


Figure 55. Superimposed GPC chromatograms of batch EL93 (red) with the PEI reference (black).

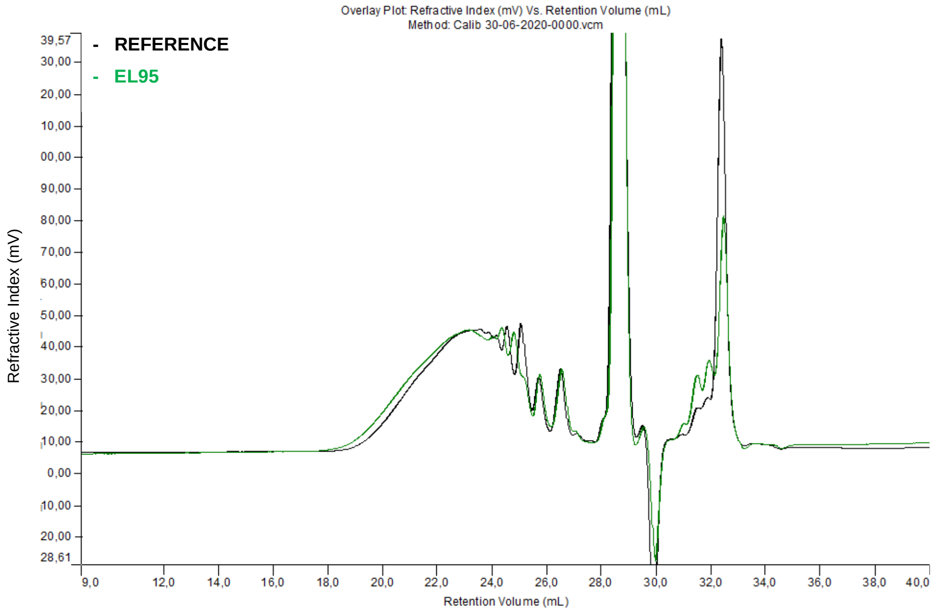


Figure 56. Superimposed GPC chromatograms of batch EL95 (green) with the PEI reference (black).

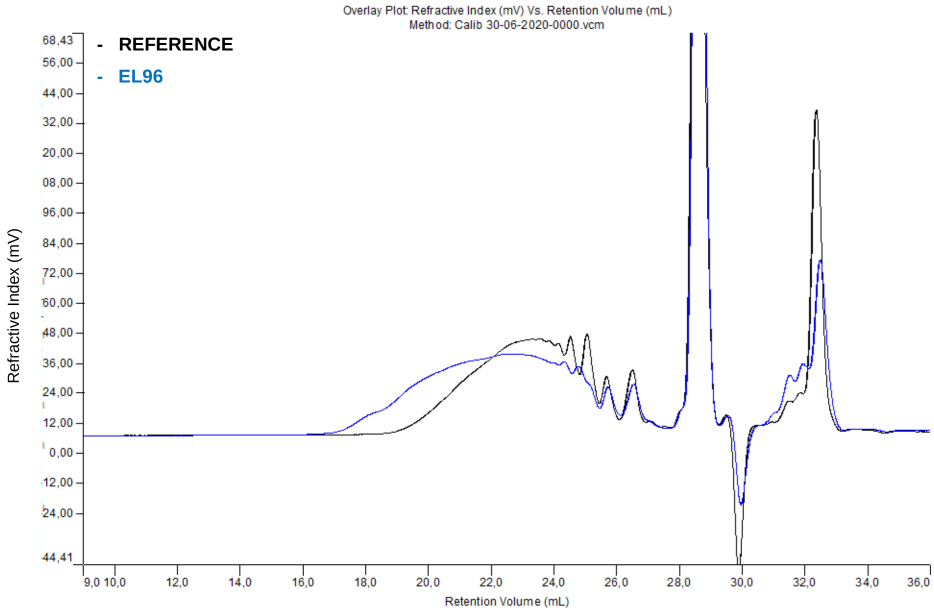


Figure 57. Superimposed GPC chromatograms of batch EL96 (blue) with the PEI reference (black).

FT-IR spectra of cured PI enamels were compared with the commercial PEI enamel (reference, red) and reported here (Figure 58).

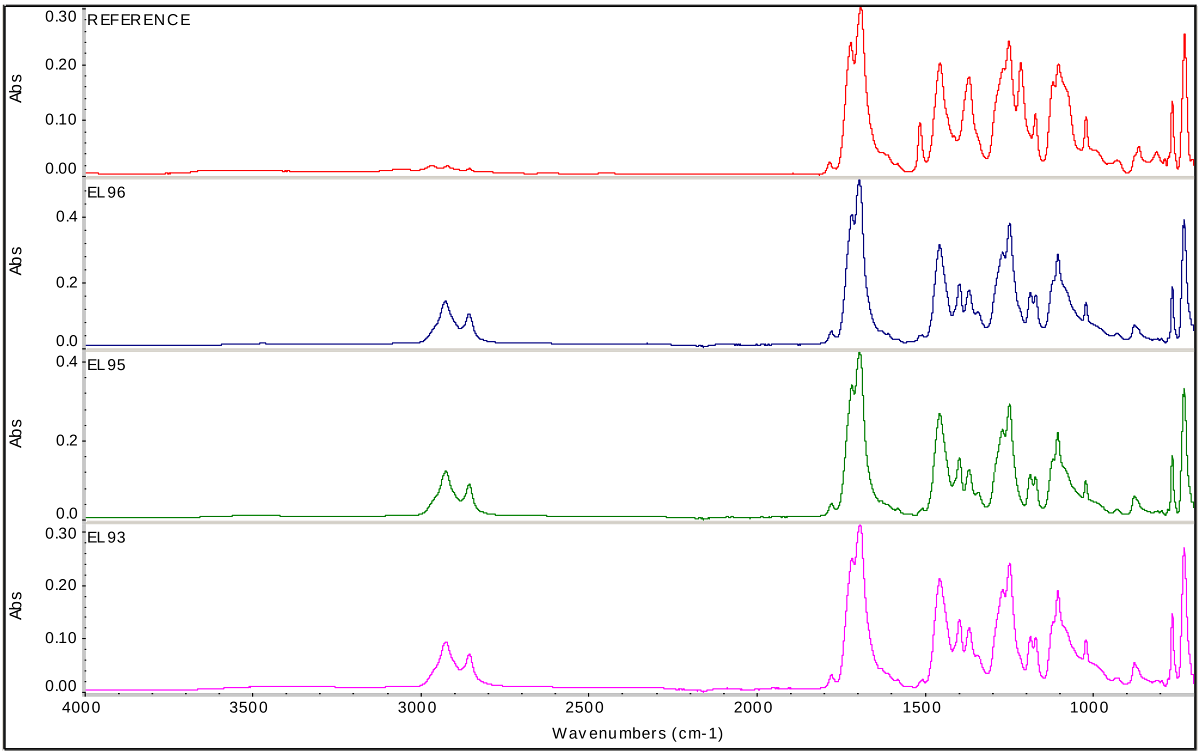


Figure 58. FT-IR spectra of cured PEIs: reference (red), EL96 (blue), EL95 (green), EL93 (purple).

Thermo-mechanical and electrical properties of cured enameled wires were evaluated and compared with a commercial PEI batch.

5.2.2. Results and Discussions

Table 32. Synthesis parameters and characteristics of the liquid resins.

	Amine	*EG distilled [g]*	*η [cPs]*	*S.C. [%]*	*Appearance*
REFERENCE	**MDA**	**20.1**	**1800-2200**	**39.0**	**good**
EL92	BD3	21.5	1780	46.3	good
EL93	BD3	57.4	1730	38.5	good
EL95	BD2	31.4	1300	44.5	good
EL96	BD1	33.2	2300	44.9	good

Table 33. Molecular weight distribution values obtained by GPC.

Batch	*Mw [g/mol]*	*Mn [g/mol]*	*Mw/Mn*
REFERENCE	**5680**	**3393**	**1.67**
EL92	6058	3597	1.68
EL93	25151	5987	4.20
EL95	6349	3543	1.79
EL96	10198	4277	2.38

Table 34. Characteristics of cured resins.

Batch	*Film aspect*	*Wire aspect*	*Jerk test*	*Flexibility [%]*	*Cut-through [°C]*	*Tgδ [°C]*
REFERENCE	**good**	**good**	**passed**	**15**	**>380**	**200**
EL92	good	good	passed	30	<190	65.2
EL93	good	good	passed	30	<190	64.5
EL95	good	good	passed	30	<190	64.6
EL96	good	good	passed	30	<190	74.1

FT-IR spectra of cured enamels of EL96, EL95 and EL93 are almost equal to each other. In all of them, the stretching absorption band for imide-carbonyl bond is observed at 1780 cm^{-1}, along with one of the characteristic imide-ring deformation band at 730 cm^{-1}, confirming the successful synthesis and curing of polyester-imides.[112] In addition, characteristic bands of the carboxylate group and the isocyanurate ring in the region between 1600 and 1800 cm^{-1} are present, and the broad band at around 3500 cm^{-1} is absent, indicating the complete curing of the PEIs.

Regarding their performances, as seen in polyimides, thermal and electrical characteristics of bio-based polyester-imides are lower than the reference due to the presence of the aliphatic moiety. In addition, no improvements were seen even increasing molecular weight of the polymer as done with batch EL93. Anyway, polyester-imides made with non-hazardous bio-based and non-carcinogenic monomers, could be used for other applications instead of wire enamels.

5.3. Conclusions

The aim of this project was to totally replace petroleum-based aromatic diamines, known for their carcinogenicity, with safer and greener raw materials.

In particular, partially bio-based and aromatic polyester-imides and polyimides were synthetized using 3 fatty acid-derived diamines, replacing 4,4'-oxydianiline (ODA). Mentioned polymers were synthetized in a polar aprotic solvent and cured on copper wires using an enameling oven. Resulting wire enamels were then tested to evaluate their mechanical, electrical and thermal characteristics.

Unfortunately, the synthesized polyimide and polyester-imide from bio-based aliphatic diamines provided a final product with lower thermal and electrical performance but improved mechanical characteristics (i.e. flexibility). Anyway, the resulting enameled magnet wires could not replace standard polyester-imide and, even more so, polyimide wire enamels. On the other hand, as seen with NMP-free enamels, partially bio-based PIs and PEIs could be used for applications where thermal characteristics are less important.

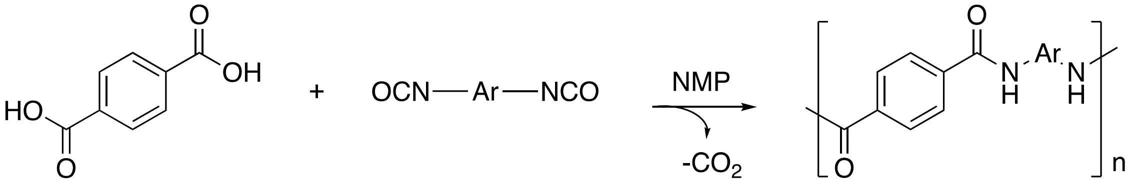
Nevertheless, the work carried out with these new materials was useful to push research towards greener solutions and to find materials that are able to meet market demands.

6. Quantitative Determination of Diisocyanates is PAIs

In the context of scientific environmentalism, the study of the possible fate of polymeric materials at the end of their life takes on considerable importance, and this depends more on the residual monomer content rather than the polymer chain. For this a novel method to stabilize and quantify residual monomeric isocyanates in high thermal resistance polyamide resins (PAs) has been developed. This new analytical method resulted in an improvement concerning the quantification of residual aromatic diisocyanates in viscous polymeric matrices by using a simple and cheap technique like HPLC-UV. Diisocyanate monomers were derivatized with dibutylamine, resulting in stable urea derivatives that were simultaneously analyzed and quantified. The method was applied to solvent-based polyamide resins, used as primary electrical insulation, for avoiding additional step of solvent removing before the analysis. The quantification of residual monomers answers to the provisions imposed by European Regulation N. 1907/2006 (REACH) for polymer registration, and the necessity of an early evaluation of the occupational risk associated to the use of diisocyanates, due to their toxicity and high reactivity with moisture.

6.1. Introduction

Polyamides (PAs) are macromolecules with repeating units linked by amide bonds. PAs have unique thermal, mechanical and electrical properties, which make them versatile products for a broad range of commercial applications.[219-220] They are important in engineering because they offer high performance at a reasonable cost, and then they are considered as one of the most versatile engineering plastics. The polyamide resins under investigation are synthetized from dicarboxylic diacids and aromatic diisocyanates through a step-growth polycondensation reaction of para-substituted AB-type aromatic monomers, carried out in a polar aprotic solvent such as N-methylpyrrolidone (NMP).[221-223] The attractive features of this reaction include the use of reactants which are tolerant of small deviations in stoichiometric equivalence, easy remove of the volatile condensate such as carbon dioxide, high yields of polymer, and generation of a wide range of aromatic polyamides.



Scheme 39. General scheme for polyamide synthesis.

The most common diisocyanates used are the mixture of isomers 2,4-, 2,6-toluene diisocyanates (TDI) and 4,4'-methylene diphenyl diisocyanate (MDI), which are both aromatic. The final product is a solvent based varnish with a viscosity range between 1000 to 3000 mPa·s, which is applied and cured at high temperature on copper wires. MDI and TDI have different chemical behaviour and confer different mechanical properties to the final product. They can be used separately, but also as a combination of the two. The industrial polymerization process reveals a lack of reproducibility and the need to add an additional amount of aromatic diisocyanates on a case-by-case basis.

At the same time, European Regulation N. 1907/2006 (REACH) imposes to the companies the registration of residual monomers, if they are present in concentration over 2% w/w, and if the monomers amount is totally over 1 ton per year. This legal obligation goes together with the ethical obligation to evaluate the residual TDI or MDI, due to their toxicological issues: isocyanates exposure is associate with occupational hazards.[224-226] In fact, in the case of wire enamel polyamides, wire enameling workers are those who are potentially at risk to diisocyanates exposure during the curing process which occurs at high temperatures during the normal production activities.[227] In addition, residual aromatic diisocyanates react with moisture, which is always present in hygroscopic solvents, giving rise to many products, including urea, oligoureas, polyureas, carbon dioxide, and aromatic amines, which are known to be mutagenic and are listed as suspected or possible human carcinogens.[228-232] These residual aromatic amines, 4,4'-methylenedianiline, could decompose with formation of aniline when heated at high temperatures in enameling ovens during the curing process.[233]

Work-related exposure to DIs can occur during the production and raw material treating, as well as in further handling with the final products, especially in the activities concerning the general coating process which is performed at high temperature. Understanding the degradation mechanism of polymeric materials that could lead to the formation of dangerous products that could lead to the formation of dangerous products for the environment is particularly useful in combating the global problem of pollution due to polymer-matrix composite materials.[234] The minimization of residual monomer content is a priority as residual monomers can result in increased hazards while representing decreased production efficiency and increased costs. It should be noted that when these low molecular weight species are considered, residual monomer must be included, but excluding other components such as additives or impurities.[235] Most of the scientific literature concerning diisocyanates analysis, covers the determination of them only as airborne contaminant in industrial environments.[236-238] Numerous methods were published that detail isocyanates analysis in polymer matrices by using fast infrared spectroscopic techniques, such as MIR and NIR, but these methodologies are widely used to monitor high concentration of diisocyanates, so they are not suitable for PAs due to the low concentration of residuals.[239] Another interesting analytical technique is the nuclear magnetic resonance spectroscopy of fluorine-19 (19F-NMR), usable modifying the isocyanate derivative with 1,1,1,3,3,3,3-hexafluoro isopropyl alcohol (HFIP).[240] Unfortunately, also in this case, quantitative magnetic resonance technique (qNMR) proves to be inaccurate due to the matrix complexity. Suitable techniques for very complex matrices, which allow determining such a low concentration of analytes, are chromatographic ones.[241] In the most suitable scientific paper found for the case under study, the authors used two techniques to determine MDI in a polyurethane foam matrix: reversed-phase high performance-liquid chromatography coupled with ultraviolet detector (HPLC-UV), and reversed-phase high-performance liquid chromatography coupled with mass spectrometry triple quadrupole detector (HPLC-ESI-MS/MS).[242] The first is widespread and easy to use technique, the latter gives a more specific response, but it is more expensive and complex. Since all the aforementioned articles refer to solid or foam polyurethane samples, we were not aware of any existing method for the determination of free monomeric DIs in solvent-based polyamide resins. Moreover, very few and aged papers reported the simultaneous quantification of residual MDI and TDI monomers. Consequently, answering to the legal and ethical obligations, we developed and applied a novel derivatization and extraction method for the analysis of both TDI and MDI for PA resin samples in the same analysis. This new method can detect free monomeric diisocyanates in the order of part per million in a polymer matrix never faced so far by using a simple and cheap technique like HPLC-UV.

6.2. Materials and Methods

6.2.1. Chemicals and materials

The 4,4’-methylene diphenyl diisocyanate (MDI) and a mixture (about 80:20) of 2,4- and 2,6-toluene diisocyanates (TDI) were provided by Elantas Europe S.r.l. and stored at -18 °C. Reagent grade triethylamine (TEA), benzylamine (BA) and dibutylamine (DBA) were purchased from Sigma Aldrich. Acetone-d6 was purchased from Sigma Aldrich.

HPLC water was purified using the Milli-Q system. HPLC grade acetonitrile was purchased from Sigma Aldrich. Technical grade acetonitrile and n-hexane were purchased from Carlo Erba. Technical grade dry tetrahydrofuran (THF) was purchased from Sigma Aldrich.

Three batches of PA were provided by Elantas Europe S.r.l. Samples have a mean viscosity of 1100 mPa·s and a mean dry content of 22.9% (solvent used is NMP). Three samples were chosen corresponding to three batches produced over a year (Table 35). One batch was marked as anomalous as a slightly greater quantity of MDI and TDI were added during the condensation phase of the production process to be able to reach the product specifications range.

Table 35. PAs sample provided by Elantas Europe S.r.l.

Sample name	***Production date***	***Abnormality***
PA 1	August 2020	Yes
PA 2	January 2021	None
PA 3	April 2021	None

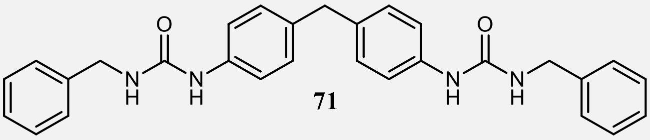
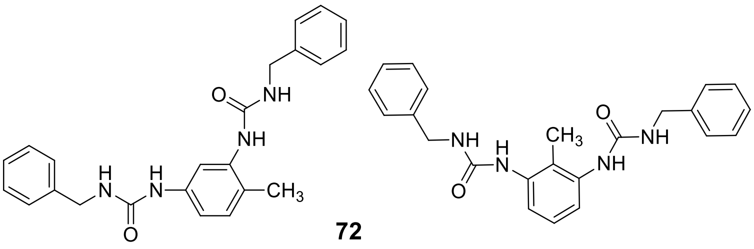
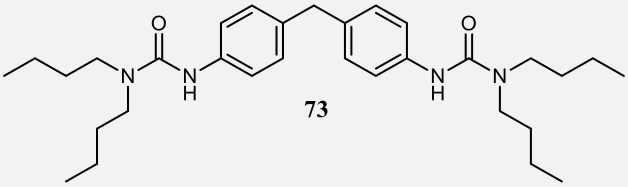
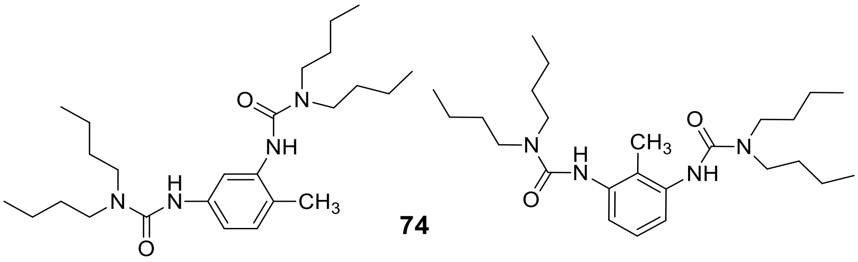
The molecular structures of the standards were confirmed by ^{1}H-NMR, recorded on a Varian Mercury plus 400 system at 400 MHz.

6.2.2. Standard preparation

DIs derivatives were synthesized following the method of Perveen et al.[243] More in detail, the monomer (10 mmol) was dissolved in 30 mL of dry THF under nitrogen flow and put in an ice bath. Then, the derivatizing agent (10 mmol) was added dropwise followed by the addition of dry triethylamine (12 mmol) and the reaction was stirred for 30 minutes at 0 °C and other 30 minutes at 25 °C. The reaction product precipitated as a white solid due to it insolubility with

THF. It was filtered and dried under vacuum. The residual white solid was purified by flash column chromatography (hexane:ethyl acetate 60:40) using Isolera™ (Biotage). Derivatization of analytes were conducted in anhydrous condition due to the strong reactivity of DIs with water. Both MDI and TDI were derivatized with two different amines, benzylamine (BA) and dibutylamine (DBA), to evaluate which resulting urea had an elution time such as not to overlap with the components of the matrix. In particular, MDI/BA-1 and MDI/DBA-3 were obtained from MDI monomer, meanwhile TDI/BA-2 and TDI/DBA-4 were produced starting from TDI monomer (Table 36). The purity of the synthetized standards was evaluated by HPLC-UV at 254 nm.

Table 36. DIs derivatization product obtained with benzylamine and dibutylamine.

Entry	*Sample name*	*Chemical structure*
1	MDI/BA-1	 **71** 1,1'-[methylenebis(4,1-phenylene)]*bis*(3-benzylurea)
2	TDI/BA-2	 **72** a b a. 1,1’-(2-methyl-1,3-phenylene)*bis*(3-benzylurea) b. 1,1’-(2-methyl-1,5-phenylene)*bis*(3-benzylurea)
3	MDI/DBA-3	 **73** *N'N''*-[methylenebis(4,1-phenylene)]*bis*(*N*,*N*-dibutylurea)
4	TDI/DBA-4	 **74** a b a. *N'N''*-(2-methyl-1,3- phenylene)*bis*(*N*,*N*-dibutylurea) b. *N'N''*-(2-methyl-1,5-phenylene)*bis*(*N*,*N*-dibutylurea)

6.2.3. Sample preparation procedure

In a 100 mL round bottom flask containing PA resin (20 g), the derivatizing agent (1 mL) and triethylamine (0.5 mL) were added dropwise at room temperature to avoid polymer precipitation. The sample was left to react under stirring for 12 hours. Hexane (5 mL) and acetonitrile (10 mL) were added to precipitate the polymer avoiding the risk of clogging the instrumentation or altering the analytes. The mixture was stirred for 12 hours and then left still for 1 hour allowing the separation of the liquid phase (containing analytes) from the polymer matrix. This procedure was repeated for all real samples, maintaining under vigorous stirring. Then, an aliquot of 1 mL of the resulting solutions was filtered before HPLC-UV analysis (Agilent™ PTFE filters 0.450 µm).

6.2.4. HPLC-UV analysis

The analysis was carried out by a HPLC apparatus (HPLC Agilent 1100 series, Agilent Technologies, Santa Clara, California, USA) using an UV detector set at 254 nm. The chromatographic separation was performed by using Luna column (C18, 150 × 4.6 mm) with 5 µm particle diameter (Phenomenex, Castel Maggiore, BO, Italy) and a temperature of 40 °C. The mobile phase was composed by solvent A, water and solvent B, acetonitrile according to an optimized gradient elution. The optimized gradient was not linear: 0 min, 50% B; 0-10 min 70% B, 10–20 min, 70% B, 20-40 min 80% B, 40-60 min 80% B; then the starting conditions were restored. The flow rate was set to 1 mL min^{-1}, the injection volume was 10 µL.

The linearity was tested in the range 0.2-10 mg/l for MDI, and 1-40 mg/l for TDI, using external calibration standards. The regression coefficient R2 were 0,9995 and 0,9999 for MDI and TDI respectively. Sensitivity was determined on the base of the limit of detection (LOD) and limit of quantification (LOQ). The LOD was assessed as the concentration at which the signal (S) to noise (N) ratio is equal to three, instead the LOQ is associated to S/N=10. MDI has 0.06 mg/l and 0.2 mg/l as LOD and LOQ respectively. TDI has 0.2 mg/l and 0.7 mg/l as LOD and LOQ respectively. LOD and LOQ values are comparable with those of the reference cited before.[242]

The precision of the overall method was evaluated by multiple analysis of real samples obtaining standard deviation in the range of 2.8-31.9%.

Accuracy was calculated on the base of the recovery values obtained by the analysis of the real sample as it is, and the same sample spiked with a known amount of MDI and TDI. Both samples were processed as independent ones, obtaining a recovery of 95.4% for MDI and 54.1% for TDI.

6.3. Results and discussion

6.3.1. DIs derivatization

DI compounds have reactive -NCO functions that must be stabilized before the HPLC-UV analysis, giving rise to the necessity of derivatization for quantitative purposes. Secondary amines are commonly used as electrophilic derivatizing agents because the obtained urea derivatives are stable and quantifiable.[244] The advantages to perform the derivatization step were the increasing of the solubility in the HPLC mobile phase of derivatives, that is related to the chemical nature of the derivatization agent, and the improving of the chromatographic efficiency, avoiding coelution with components of the matrix. The latter is particularly important when a non-specific detector like UV is used. In this work two different amines were tested: an aromatic one such as BA, and an aliphatic amine like DBA. BA had the adding value of increasing the response of the correspondent derivative at the detection wavelength, due to the presence of an additional aromatic moiety able to respond at 254 nm. On the other side, the latter secondary amine had the advantage to improve the derivative solubility in the mobile phase. BA and DBA derivatives were synthetized and purified in our laboratories, then their solubility in the mobile phase used for the chromatographic separation was checked. Unfortunately, urea MDI/BA-1 was discarded due to its poor solubility in the eluent solution constituted by acetonitrile and water at a concentration of 1 mg/mL. The poor solubility could be explained due to presence of about 78% of NMP (NMP solvent for PAs matrixes). A subsequent step was testing the urea derivatives in the chromatographic condition in the presence of the matrix to evaluate detrimental overlap with matrix components. Urea TDI/BA-2 demonstrated to coelute with interfering species and cannot be used for quantitative purposes using UV detector system. Instead, both DBA derivatives of MDI and TDI revealed a good solubility in the mobile phase and retention times compatible with the other signals coming from the matrix. For this reason, the PA samples were derivatized with DBA.

6.3.2. DIs quantification in PAs samples

The developed analytical method was applied to PA samples manufactured by Elantas S.r.l. company. Three batches produced in different seasons were analyzed in order to evaluate the residual monomers MDI and TDI, in addition to the reproducibility of the industrial polymerization reaction. In fact, the high reactivity of DIs, especially in the presence of moisture in the reaction solvent, gave rise to a lack of standardization of the polymerization process. For this reason, it is a common practice to follow the polymerization reaction by monitoring the viscosity from time to time. If the viscosity, at the end of the production process, is under the stated specification, higher amount of monomers is used by subsequent addition. This is the case of the PA1 sample belonging to the batch produced in August 2020, that is labelled as anomalous. On the contrary, PA2 and PA3 samples were the results of a standard process. The results are reported in table 3. The analyses revealed a residual amount of MDI in the range 0.3 - 1.7 mg/kg. Instead, higher concentration of TDI monomer were found in all samples, registering a concentration between 9.1 mg/kg and 28.4 mg/kg. The anomalous sample demonstrated levels of monomers comparable with the standard ones, indicating that the additional amount of monomers used during the process didn’t affect the quantity of residual monomers. Moreover, the residual monomers were largely lower of 2% w/w in all analyzed samples, that avoid the registration activities according to the REACH Regulation.

Standard deviation % is pretty high in PA1 and PA2 for MDI determination and in PA2 for TDI determination. This is explained by the strong interferences that are present in the sample matrix that make the background signal very irregular compromising an exact integration of the peaks of the analyte signal.

Sample		*MDI*		*TDI*	
		Mean conc. [mg/kg]	DEV. STD %	Mean conc. [mg/kg]	DEV. STD %
PA 1	August 2020	1.7	31.9	9.1	2.8
PA 2	January 2021	0.3	17.7	28.4	14.5
PA 3	April 2021	1.0	7.0	9.5	3.0

6.5. Conclusions

In the present manuscript we developed a new and general analytical method able to determine residual monomeric aromatic isocyanates in many consumer products in which one of their primary raw material ingredients are diisocyanates. Although identifying and quantifying the content of aromatic isocyanates would be possible by several analytical methods, but each is highly specific and is labor intensive and expensive. Our method allows to analyze easily and quickly the common aromatic used-diisocyanates, such as toluene diisocyanate (TDI) and methylene methane diisocyanate (MDI). For the first time, the optimized analytical method revealed good accuracy and precision over the concentration range 0.3 - 1.7 mg/kg of MDI, and 9.1 - 28.4 mg/kg of TDI resulting from the analysis of PAs real samples, thanks to the derivatization method studied, through which it is possible to extract the analytes from the polymer matrix and analyze them.

The results obtained from this analysis indicate that the batch where an additional amount of monomers were added during the production process (labelled as anomalous) does not prove to have an abnormal concentration of diisocyanates compared to the other batches. In addition, there is no evident correlation between the storage time of the batch and the concentration of residual monomers in it. Therefore, it is logical to think that this new analytical method could be useful for further analyses in similar matrices as solvent-based polyamide-imides (PAIs) and polyamic-acids (PAAs) which are easily synthesized by polycondensation of aromatic diamine with dianhydride, in order to avoid any health issue due to the high temperature used for their production. Furthermore, even more important is that the method finds application in viscous polymeric matrices, and therefore it suggests its use for the determination of residual isocyanates in medical devices.[245] In these consumer products complex analysis determinations of keratin-isocyanate adducts are required since isocyanates react instantly with skin components. The method was studied for aromatic isocyanates because it is known that they are much more dangerous than the aliphatic correspondents.[246]

Further studies are underway to improve this method especially to lower the percentage standard deviation.

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